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Accelerated Carbonation for the treatment of MSWIr: Optimisation and Reaction Modelling

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A thesis submitted for the degree of Doctor of Philosophy of the University of London

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A mi familia Marta, Jose Antonio y María

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ABSTRACT

Moist calcium silicate minerals are known to readily react with carbon dioxide (CO_2). The Accelerated Carbonation of hazardous wastes is a controlled accelerated version of the naturally occurring process. The solid mixture is carbonated under a gaseous, CO_2 rich environment at slightly positive pressures (~3 bar), which promotes rapid stiffening of the non-hydrated product into a structural medium within minutes. In addition, an increased binding of toxic metals occurs as the solid carbonates. Today, Accelerated Carbonation is a developing technology, which may have potential for the treatment of wastes and contaminated soils and for the sequestration of CO_2, an important greenhouse gas. The consequent significant improvement in the properties of certain treated materials can facilitate reuse in a variety of construction applications. Accelerated Carbonation represents a potential solution to sustainable waste management, the problem of decreasing landfill space in the UK, rising CO_2 emission levels and the depletion of natural aggregate resources.

This thesis reports on the application of Accelerated Carbonation for the treatment of Municipal Solid Waste Incinerator residues (MSWIr). The treatment imparts chemical and mineralogical changes to the residues, which reduce their environmental impact through encapsulation of hazardous components and cementation by carbonate precipitation.

Given the viability of carbonation as a process to treat MSWIr, this investigation focused on optimising the fundamental parameters determining the extent and quality of carbonation of these residues. Major attention was also given to the modelling of the kinetics and mechanism of the carbonation reaction of Air Pollution Control Residues (APCr). The kinetics were studied in a batch carbonation rig designed and built at University College London. In addition, the major physical and chemical changes in APCr and Bottom Ashes (BA) after carbonation were evaluated using various analytical techniques.

In addition, a commercial feasibility study has been carried out which confirmed the considerable and immediate potential for the commercialisation of Accelerated

Carbonation technology for the treatment of municipal MSWIr. This conclusion was reached by analysing the market and industry for waste management, competing innovations and the capacity of Accelerated Carbonation to enable the recycling and reuse of CO_2 and solid wastes.

This work provides a fundamental understanding of the Accelerated Carbonation reaction of APCr essential to further ascertain the scale-up parameters required for the design of a large scale continuous process.

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NOTATION

Cement nomenclature: C CaO calcium oxide

S SiO_2 silicon oxide

H H_2O water

$\bar{S}$ SO_4^{2-} sulphate

A Al_2O_3 aluminate

$\bar{C}$ CO_2 carbon dioxide

a stoichometric coefficient [–]

b stoichometric coefficient [–]

d diameter [m]

k, k_i rate constant [s^{-1}]

k_m mass transfer coefficient [m/s]

m order of reaction [–]

n order of reaction [–]

r_A rate of reaction [mol/s m^2]

r radius [m]

s stoichometric coefficient [–]

s.d. standard deviation [–]

t time [s]

$t_{0.5}$ reduced time [s]

v volume [m^3]

w weight [kg]

w/s water-to-solid ratio [–]

w/c water-to-cement ratio [–]

x conversion [–]

y stoichometric coefficient [–]

z ratio molar volume of product to molar volume of reactant [–]

A frequency factor or pre-exponential factor [s-1]

C concentration [mol/l]

D	diffusion coefficient [m^2/s]
E_A	activation energy [Jul/mol]
P	pressure [$kg/m \cdot s^2$]
P_f	compaction pressure [kg/m^2]
P_{CO2}	partial pressure of CO_2 [$kg/m \cdot s^2$]
Rc	strength [kg/m^2]
R	universal gas constant [8.314 $kg \cdot m^2/s^2 \cdot K \cdot mol$]
R^2	correlation coefficient [–]
T	temperature [°C, K]
V	volume [m^3]

Greek letters:

α	degree of transformation or fractional reaction [–]
β	nucleation factor [–]
ε	voidage [–]
λ	dimension factor [–]
τ	time for complete conversion [s]

Subscripts:

aq	aqueous
e	effective
p	particle
s	surface
v	volume
A	gas
C	core
S	solid
0	initial

CHAPTER 1

1 Introduction

The successful research and development of a new technology to generate new materials or components using waste as the raw material is a very complex task. Since the main controlling variables are technological, business and regulatory, this task requires a multidisciplinary approach involving knowledge from different areas such as material science, geology, environmental sciences, chemical engineering and legal and business awareness.

The development of sustainable waste management technologies is a major concern nowadays. Recent estimates show that the waste management market in the UK will double between 2002 and 2012 to reach £11bn [1]. Municipal Solid Waste (MSW) is one of the major solid waste streams. Landfilling and incineration are the preferred routes to dispose of this waste. The latter is increasingly becoming the most popular option for disposal of MSW as landfill space decreases.

Incineration is more common in countries like Switzerland, Japan, France, Germany, Sweden and Denmark, where the space for landfilling is limited. These are countries in which ~50% of the MSW is being, or will be, incinerated. In the USA only 16% of the MSW is being incinerated. Over 80% of MSW is directly disposed of in landfill sites in the UK. Approximately 10% of MSW is recycled and a further 10% is incinerated.

Currently there are 30Mt of MSW being produced per year in the UK and this amount is steadily increasing. The prospects are that this amount will double by 2020 [2]. Incineration results in two other unwanted solid streams, Bottom Ash (BA) and Air Pollution Control residues (APCr). The wastes produced from incineration (~3.0Mt/yr) are landfilled to a large degree (80% of the BA and 88% of the APCr), though some are processed and reused as secondary aggregates [3].

Some 50% of the APCr are deposited at a single ash landfill and the reminder goes to co-disposal landfills. As a reaction to this problem, there is an increasing legislative pressure to reduce landfilling in the UK in the face of increasing solid waste volumes.

The requirements imposed by the Landfill Directive 1999/31/EEC that are relevant to the disposal of MSW and MSWIr are the following [4]:

- compulsory treatment of all wastes prior to landfill
- strict classification of landfill sites to dispose of: hazardous, non-hazardous (incl. MSW) and inert waste. Landfill sites have to comply with numerous criteria to ensure quality of leachate.
- reduction of the amount of biodegradable MSW that goes to landfill over a 15 year period, to 35% of the amount produced in 1995
- a ban on co-disposal of hazardous and non-hazardous wastes

There has been a substantial amount of research on the characteristics and treatment of MSWIr, the short and long term leaching performance, effect of weathering on this performance and disposal strategies. Given the stated limitations on landfilling, the preferred alternatives to dispose of MSWIr have become stabilisation/solidification [5, 6], reuse in concrete manufacturing [7, 8], carbonation [9, 10] and acid neutralisation [11].

In a recent study by the Environment Agency (November 2004) carbonation and acid neutralisation were selected to analyse their effects on the leaching behaviour of MSWIr. A study concluded that carbonation is the most promising alternative to treat MSWIr, with the hazardous properties being alleviated by carbonation due to consumption of lime and precipitation of calcite. The pH is reduced without significant loss of acid neutralisation capacity (ANC), thereby buffering pH and controlling the solubility of major heavy metals [12].

Simultaneously, there is broad agreement that the Earth's climate is changing and that this is linked to a build up of greenhouse gases in the atmosphere enhancing the natural greenhouse effect. Carbon dioxide (CO_2) is the most significant of these greenhouse gases in terms of quantity. The effect on the climate will

increase significantly if concentrations of CO_2 in the atmosphere exceed around 550ppm. To stabilise CO_2 concentrations at or below this level over the next 100 years will require global emissions reduction (relative to the 2003 levels) of 50 to 60% by 2050. The UK government committed itself to that target on February 2003 following the recommendations of the Royal Commission on Environmental Pollution [13].

In order to achieve these targets, the development of a portfolio of technologies and policies will be required. Thus, substantial effort is being put into developing economic methods to dispose of CO_2. One possibility is to capture and then store the CO_2 in geological structures, saline aquifers, depleted oil and gas wells or in materials. As an example of the last of these, the present work studies an innovative technology known as *accelerated carbonation*. The CO_2 is chemically stored in materials as solid carbonates. The fundamental advantages of this route are that the resultant products are thermodynamically stable and therefore the sequestration of CO_2 is permanent and safe.

Carbonation is a natural phenomenon affecting commonly used cementitious materials and may have detrimental effects on structural concrete. On the other hand, carbonation has been demonstrated to act positively in the immobilisation of heavy metal-contaminated soils and other residues [14-18]. Carbonation is able to stabilise alkaline inorganic wastes, generating geochemically stable species, with potential to be used as secondary aggregates.

The accelerated carbonation of certain hazardous wastes containing CaO/MgO is a controlled accelerated version of the naturally occurring process. The solid mixture is carbonated under a gaseous, CO_2 rich environment at slightly positive pressures (~3 bar), which promotes rapid stiffening of the non-hydrated product into a structural medium within minutes. In addition, an increased binding of toxic metals occurs as the reaction progresses. The consequent significant improvement in the chemical and physical properties of certain treated materials can facilitate reuse in a variety of construction applications.

It can be seen that accelerated carbonation provides a solution to the problems of depleting natural aggregate resources and the decreasing number of landfill sites in the UK, through the recycling of wastes. In addition, CO_2 is stored through conversion to solid carbonates. At a time when rapidly changing legislation is forcing the recycling and reuse of waste materials, the emergence of a technology that has the major advantage of permanently binding CO_2 and at the same time upgrading waste material into re-useable materials is timely.

Given the feasibility of carbonation as a process to treat MSWIr, this thesis focuses on the optimisation of the fundamental parameters determining the extent and quality of carbonation of these residues. Major attention is also given to the modelling of the kinetics and the mechanism of the accelerated carbonation reaction of APCr. The kinetics were studied in a batch carbonation rig. In addition, the major physical and chemical changes in APCr and BA after carbonation were evaluated.

In parallel, a study of the commercial feasibility of accelerated carbonation was carried out as part of the New Technology Ventures course at the London Business School. The outcome was an assessment of the business opportunity and a set of recommendations to commercialise accelerated carbonation. Competing innovations were compared and the most economically viable and sustainable business model for implementation among the various options was identified.

1.1 Objectives and Structure of the Work

Research into accelerated carbonation at the University of Greenwich started approximately ten years ago. Currently it has developed into a unique structure for collaboration between two research groups, the Centre for CO_2 Technology in the Department of Chemical Engineering at University College London and the Centre for Contaminated Land Remediation in the School of Earth and Environmental Sciences at the University of Greenwich. The principal objective of the joint project is to investigate and optimise the potential for accelerated carbonation of silicate-based municipal wastes using waste CO_2 gas to produce artificial construction aggregates on a large scale and continuous basis.

The objective of the work presented in this thesis is the optimisation of the major parameters governing accelerated carbonation of MSWIr and the modelling of the kinetics of accelerated carbonation reaction of APCr.

The group which is providing a multidisciplinary approach to the environmental problems described above incorporates three PhD students and three academics. One PhD project focuses on studying the short and long term chemical properties of the MSWIr after carbonation, with particular interest in the leaching behaviour and the potential to produce reusable artificial aggregates. A second PhD project consists of investigating the suitability of fluidisation to scale-up the accelerated carbonation process. The third PhD project is the work presented in this thesis. The aim of the joint project is to develop a commercially feasible technology that sequesters CO_2 and transforms waste material into useful products, providing a sustainable approach to waste management.

As a first step, an in-depth literature review was conducted on carbonation. The effects of the accelerated carbonation reaction on the solid phase, the adopted techniques for different materials, recent developments and future potential applications of this technology were considered. Furthermore, the parameters controlling the process and the broad range of materials susceptible to carbonation were discussed. This is reported in Chapter 2.

As a second step more than a hundred UK thermal residues included in the European Waste Catalogue were studied regarding their suitability for carbonation. On the basis of the volumes produced, the degree of hazard, the morphology and chemistry of the residues and their extent of carbonation, Power Station Ash (PFA), Blast Furnace Slag (BFS), and MSWIr were selected for closer analysis. BFS was disregarded due to previous experience carbonating steel slags. As for the PFA, they are reused in the construction industry and due to their harmless nature and low lime content, there is no need of any pre-treatment. However, MSWIr showed a much higher extent of carbonation. In addition, the increased volumes and the favourable characteristics made them the selected target for the carbonation process. This is reported in Chapter 3.

The third step involved experimental work to optimise the carbonation potential of the MSWIr and elucidate the optimum process conditions and the optimum sample preparation. This work was carried out with ashes from different MSW incinerators throughout the UK using the carbonation rig at the University of Greenwich. The effects of carbonation on the physical and chemical properties of the MSWIr were investigated experimentally using different techniques. The changes in mineralogy and microstructure were also studied.

The fourth step was an investigation focused on carbonation of APCr in the experimental rig at University College London. A reaction model was chosen and the controlling mechanism of the accelerated carbonation was ascertained. Prior to that, a comprehensive study of the background theory to model the kinetics of carbonation of APCr was carried out. This is reported in Chapter 4. Chapter 5 describes the materials, equipment and experimental methods. Several sets of experiments varying the carbonation conditions were undertaken in order to determine the kinetic model of the carbonation reaction. This stage involved the determination of the 'kinetic triplet', the Arrhenius parameters and the order of reaction. With the help of analytical experiments the mechanism of reaction was elucidated. This is reported in Chapter 6.

The final step involved a commercial feasibility study to asses the business opportunity for accelerated carbonation. The options for the commercial application of carbonation to a number of different markets were studied and the key customer group was found. Major competing innovations were compared and carbonation was found to have superior characteristics. Subsequently, the most economically viable and sustainable business models were analysed. This is reported in Chapter 7.

This work provides a fundamental understanding of the accelerated carbonation reaction of APCr essential to further ascertain the scale-up parameters required for the large scale, continuous process.

Figure 1-1 shows the stages and decisions in research on accelerated carbonation.

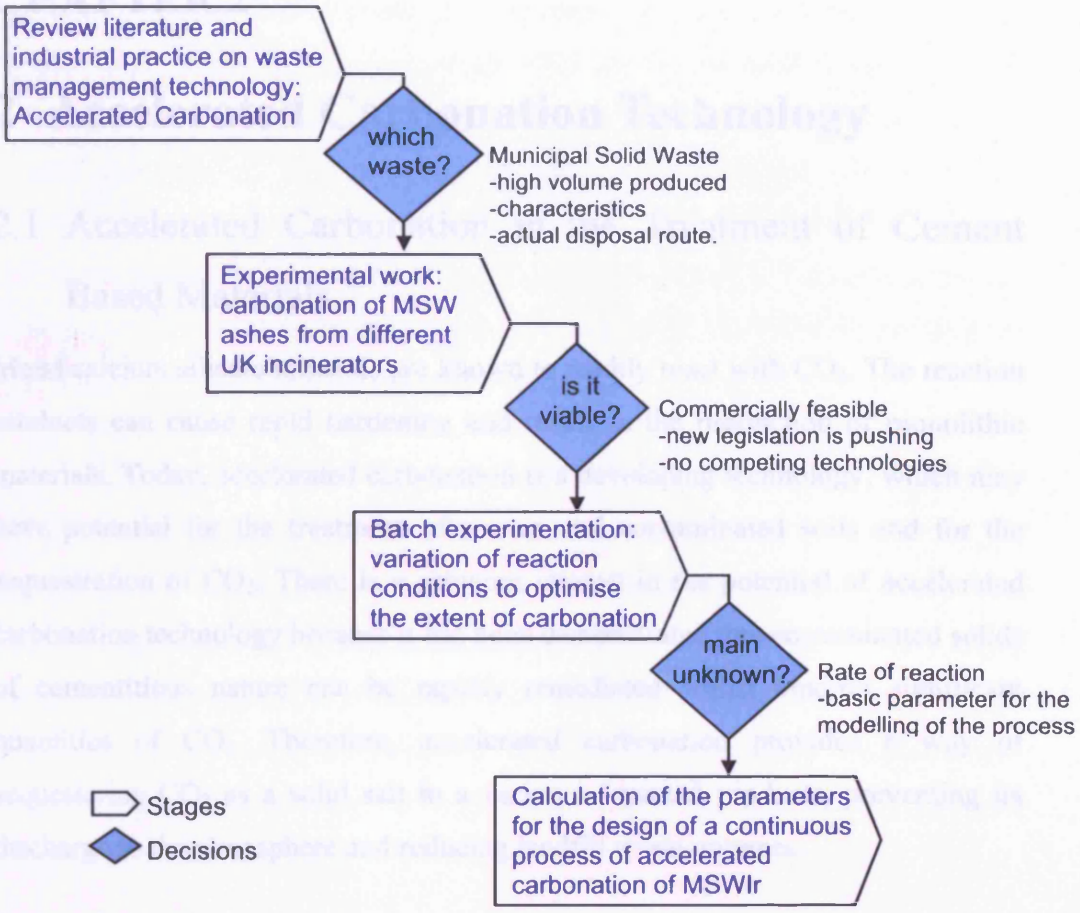

Figure 1-1 Stages and decisions in research on the accelerated carbonation process

CHAPTER 2

2 Accelerated Carbonation Technology

2.1 Accelerated Carbonation in the Treatment of Cement Based Materials

Moist calcium silicate minerals are known to readily react with CO_2. The reaction products can cause rapid hardening and result in the production of monolithic materials. Today, accelerated carbonation is a developing technology, which may have potential for the treatment of wastes and contaminated soils and for the sequestration of CO_2. There is a growing interest in the potential of accelerated carbonation technology because it has been demonstrated that contaminated solids of cementitious nature can be rapidly remediated whilst binding significant quantities of CO_2. Therefore, accelerated carbonation provides a way of sequestering CO_2 as a solid salt in a variety of treated products, preventing its discharge to the atmosphere and reducing landfill waste volumes.

2.2 Applications of Carbonation

2.2.1 Natural Carbonation

The utilisation of natural carbonation for the formation of carbonated cementitious systems is not new. Man has used alkaline earth hydroxide cements and mortars, which harden due to their reaction with atmospheric CO_2, for thousand of years. However, the development of strength in these calcareous cements is slow and uneven due to the low partial pressure of CO_2 in the atmosphere (which is only 0.03-0.06% v/v), and the slow rate of diffusion of CO_2 into mortar [19].

In service, Ordinary Portland Cement (OPC) based materials are usually exposed to percolating ground water or infiltrated rainwater and are therefore subject to corrosion. If the water contains CO_2, the effect is that carbonic acid neutralises the

alkalis in the pore water. The calcium silicate hydrate gel (C-S-H[1]), which is the dominant hydration product resulting from normal hydration of OPC, is dissolved by the acidic environment, consequently affecting the leachability characteristics and the durability of cementitious products over time. As acid attack proceeds, a considerable amount of dissolution of primary cementitious phases results, together with the precipitation of secondary phases. The main secondary mineral, $CaCO_3$, is formed by the combination of moist CO_2 with Ca^{2+}, mobilised via the dissolution of calcium hydroxide (portlandite) and from the decalcification of the gel phase, C-S-H, to leave silicate hydrate [20].

2.2.2 *Effect of Carbonation on the Durability of Hardened Cement Based Products*

Reinforcement corrosion is the most important durability problem of structural concrete. In general, the cement present in the concrete hydrates, giving a highly alkaline medium (ca. pH 13). This confers a chemical protection to steel through a passive protective oxide film, formed in an environment at or above a pH of 10.5. Carbonation of concrete can destroy this passive oxide film, leaving the steel exposed to corrosion [21].

2.2.3 *Accelerated Curing of Compacted Cementitious Systems by Carbonation*

When applied to compacted systems, such as mortars, carbonation takes place mainly in the outer portions of monoliths. The initial reaction on exposure to CO_2 appears to be an accelerated hydration of the silicates to form a C-S-H-like gel and calcite. After 3 minutes of carbonation the amount of C_3S reacted is similar to that after 12h of hydration [22].

The stoichometry of the initially formed C-S-H gel is similar to that found in conventional hydration. Further reaction results in progressive carbonation of the gel with the consequent decrease in its content of calcium oxide. However, the strength development in the compacted mortar exposed to CO_2 is much more rapid than during normal hydration [22] and experiments have shown that a load

[1] Nomenclature used in this work: C=CaO, S=SiO_2, H=H_2O, $\overline{S}$=SO_4, A=Al_2O_3, $\overline{C}$=CO_2

bearing capacity of approximately 1000 kg/cm^2 (100 MPa) can be obtained within 15 min in carbonated Portland cement paste, confirming the potential of carbonation to accelerate the hardening of thin-walled materials [23].

2.2.4 Carbonation as a Stabilisation/Solidification Technique

Cement-based solidification using hydraulic or pozzolanic binders is used for the immobilisation of soils and sludges containing a variety of metal pollutants. Solidification with cementitious materials is attractive because it offers an assurance of chemical stabilisation (at high pH) of many compounds and produces a mechanically stable waste form. It is a recognised way of disposing of solid wastes and even water contaminated with toxic heavy metals [24].

Solidification can be defined as the chemical binding process that binds toxic waste matter into solid bulks or physically cuts them off from the outside by forming a capsule. It is a process that converts potentially toxic waste materials into less toxic solid materials before landfilling [25]. The choice of binder is a balance between cost and environmental considerations. The more C_3S or calcium the binder contains, the higher the potential for producing a carbonated product.

In the UK over three-quarters of the waste produced in the Thames Region, including London (the largest producer of waste), ends up in landfill sites. This amounts to 22 million tonnes per year and comprises household, industrial and commercial waste streams. It is estimated that the landfill sites for the South East of England will be at full capacity by 2005 and problems with leaching will occur. Furthermore, legislation restricting disposal to landfill is driving the growing interest in stabilisation/solidification for re-cycling certain waste materials, including the products of incineration [26].

2.2.4.1 Stabilisation of Wastes by Carbonation

Cement-solidified hazardous wastes are susceptible to carbonation. Carbonating the solidified waste before landfill lowers the pH to values corresponding to the minimum solubility of many heavy metals and to within regulatory defined limits (pH <9.5). This leads to general improvements in metal immobilisation. However, the reduction of the buffering capacity of the solidified matrix due to the lowered alkalinity, makes the waste more vulnerable to the effects of acid attack and, hence, to the release of heavy metals in the long-term [27], especially where open containment systems are employed. Carbonation also increases the ANC of the material under acidic conditions. For instance, the ANC of BA increases from 0.46-0.48 meq/g to 0.88 meq/g (at pH 5) after 48 h accelerated carbonation [28]. Carbonation of cement-waste mixtures leads to changes in the microstructure, increases the strength values (based on non-confined crushing tests) by up to 70% and can decrease the leaching of metals. Materials that have been utilised in either laboratory or pilot-scale evaluations using accelerated carbonation technology are shown in Table 2-1.

Waste	Description	Usual disposal routes
Slags	Secondary products from metal refining.	Aggregate manufacturing.
BFS	Granulated blast furnace slag.	Cement production and concrete admixture.
SS	Steel production.	Amour stone and soil conditioning.
Galligu	By-product of the manufacture of sodium carbonate.	Dumped to pits and covered with ash.
MSWI Ash	Ash from combustion of municipal solid wastes. There are two kinds, bottom and fly ashes.	Disposed of in landfills. Incorporation into materials for construction applications.
Deinking ash	Ash from paper recycling process.	Dumped to landfill.
Cyclone dust	Air Pollution Control waste.	Landfilled.
Cupola furnace dust	Waste dust coming from furnace for metal casting.	Landfilled.
Filter cake	Residue deposited on a permeable medium when a slurry is forced against the medium under pressure.	Landfilled in general. Certain treatments depend on the nature of the cake.
Pulverised fly ash	Powder of burnt coal in thermal power stations.	Additive in the building industry.
Cupola arrester filter cake	The insoluble residue deposited on the air pollution control devices of a cupola furnace.	Landfilled.
Sewage Sludge Ash	By-product produced during the combustion of dewatered sewage sludge in an incinerator.	Landfilled, concrete production, mineral filler and soil conditioner.
Sewage sludge	Waste product from wastewater treatment.	Stabilisation with cement.
Cement kiln dust	Partially calcined mineral mixture.	Landfilled. Agricultural applications.
Air Pollution Control Residues	Combined material collected either in electrostatic precipitators or fabric filter devices.	Landfilled and used for cement production.
Coal Fly Ash	Residue coming from coal burning power plants.	Cement products and landfilled.
Arc Furnace Dust	Largest solid waste stream produced by steel mills.	Recycled and landfilled.
Thermal reclaim dust	Dust coming from the breaking of the sand treated in the reclaim units for its reuse in casting processes.	Used as fillers, for concrete manufacturing, for asphalt manufacturing.
Fettling shop extraction dust	Dust coming from the lining of castings in a furnace.	Recycled in-plant and landfilled.
Shot-blast dust	By-product from the cleaning of finished castings.	Used as roadbase and the rest landfilled.
Bag-house dust	Bag-house dusts are collected from emissions from the furnace or sand reclamation plant.	Landfilled. Used as raw material for cement and concrete manufacturing.
Foundry sands	By-product of the foundry casting process of metals.	Partly re-used and partly landfilled.
Blast furnace flue dust	Filter sludge from wet cleaning plants from foundry, iron and steel industries.	Part recycled, and the rest sent to landfill.
Melting dust	By-product of the molten metal injection processes.	Mostly recycled.
Mill scale	Filter dust from sand regeneration and fettling shop plants.	Landfilled and recycled.
Silica pot liner	Waste product of the electrolytic process in the smelting of aluminium.	Vitrified, and landfilled.
Coke breeze	Filter dust from hall dust extraction plants.	Mostly recycled and the rest landfilled or land applied.

Table 2-1 Wastes that have been treated by carbonation and their usual disposal routes [29]

The carbonation of solidified low-level radioactive wastes has also been studied. It has been found that some radionuclides pass through the carbonated zone and may react forming a solid solution[2] with calcite [31].

2.2.4.2 Stabilisation of Contaminated Soils by Carbonation

The contamination associated with derelict land can also be treated using waste CO_2. By using CO_2 gas at atmospheric or slightly positive pressure and carbonating with it a mixture of the contaminated soil and an appropriate binder, the reaction can be carried out within a few minutes. Suitable binders are Portland cement, quick lime, slaked lime and a variety of waste products, including slag. In addition, there are naturally occurring calcium silicate minerals that also have potential for carbonation [32], making it a process with low environmental impact.

The major advantage of this treatment over conventional solidification/stabilisation systems, in which long curing time may be required, is that with carbonation the soil is immediately available for development. It can be applied on-site and the soil develops almost immediate high strength and low pH characteristics, consequently reducing costs. In addition, accelerated carbonation is a versatile process, which can be used in conjunction with other treatment techniques to treat organic as well as inorganic contamination on a variety of scales [33].

The carbonation technique underwent successful pilot-scale field trials for the first time in September 2000 when accelerated carbonation was applied at an ex-pyrotechnics site at Dartford in Kent [34]. Soil on the site had general elevated levels of heavy metals, with isolated contaminant hotspots across the site [35].

Following the Dartford trial, a subsequent series of trials were carried out and the results have been reported. These results are summarised in Table 2-2.

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[2] A solid solution is defined as the compositional variation resulting of an ion or ionic group for another ion or ionic group. This solid-state-solution is considered a solution rather than a compound when the crystal structure of the solvent remains unchanged by addition of the solutes, and when the mixture remains in a single homogeneous phase [30].

Site	Soil contaminant	Result
Galligu landfill, Widnes	Alkaline waste rich in $Ca(SO_3)_2$	Successful. Soil converted to aggregates. Heavy metal concentration reduced.
Cement kiln dust deposits, Kent	Flue dust, partially calcinated mineral mixture and rich in heavy metals.	Inconclusive. Leachate quality improved except for sulphate.
Domestic and industrial landfill, Derby	Oils, tars, cyanides, phenols, heavy metals, NH_4, Br.	Poor results. Increase in granularity and durability. Heavy metals are mobilised.
Former site of chemical plant, Chesterfield	Coal tars, lime sludge, acids, phenols, cyanides, VOC, Spent oxide, ammoniacal wastes, S, heavy metals and asbestos.	Inconclusive. Most heavy metals are immobilised.
Oil-based drill cutting, Birmingham	Oil and bentonitic clay, high level of barium salts, organic matter and soluble salts.	Successful. Soil converted into semi-granular soil. Soil complied non-hazardous waste requirements.

Table 2-2 Summary of results of trials to contaminated sites [33]

2.2.5 Recycling of Waste Streams

Accelerated carbonation reactions can also be suitable for the treatment of non-hazardous waste streams, to improve their reuse in some way. For instance, powdered materials with appropriate chemical properties and high surface areas for reaction could be solidified to produce useful products.

A known application is the recycling of concrete waste produced by demolition of concrete structures. Through carbonation the waste is consolidated and a solid material with greater strength is produced [36].

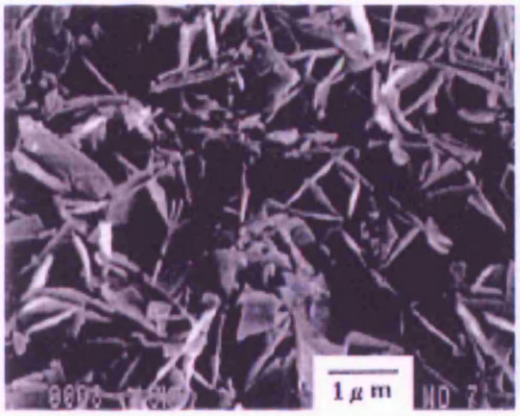

Figure 2-1 (a) Non-carbonated autoclaved light weight concrete [36]

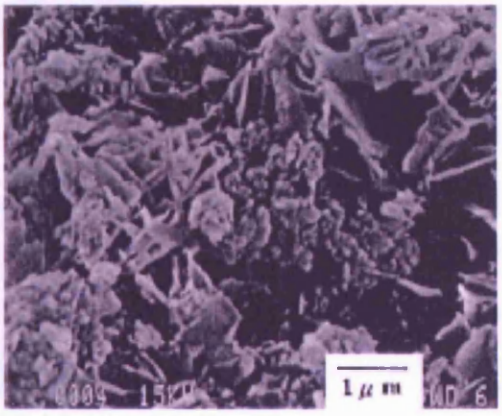

Figure 2-1 (b) Carbonated autoclaved light weight concrete [36]

Figure 2-1 shows SEM images of concrete samples before and after carbonation. The image of the treated sample (Figure 2-1 (b)) shows the granular-textured calcite that has precipitated between the plate-like particles of the initial mineral and a higher density can be appreciated. Regarding the recycling of hazardous and non-hazardous wastes, if treatment by accelerated carbonation is to be considered, a number of factors have to be evaluated, including the durability of the treated product and the reuse options defined under current law.

2.3 Process Requirements and Reactions for Accelerated Carbonation

For a solid to be suitable for accelerated carbonation, it must have certain chemical and physical properties that make it appropriate for treatment.

2.3.1 Definition of the Carbonation Reaction

Ionised CO_2 induces solvation of calcium ions from the solid phases, which then re-precipitate in the pore space of the mixture as $CaCO_3$, forming a solidified product [37]. This process is exothermic.

The reaction is diffusion controlled. The gas diffuses into the porous solid resulting in a growing ring of carbonated material surrounding an inner zone of non-carbonated material. The conceptual model for the reaction of CO_2 with a wasteform is presented in Figure 2-2.

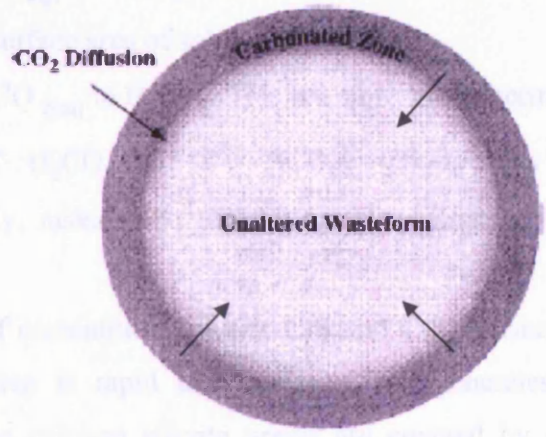

Figure 2-2 Schematic of carbonation process [17]

2.3.2 *Reaction Mechanism*

The following is the sequential mechanism that takes place during the carbonation of cementitious materials. Figure 2-3 illustrates this mechanism, showing all the individual steps:

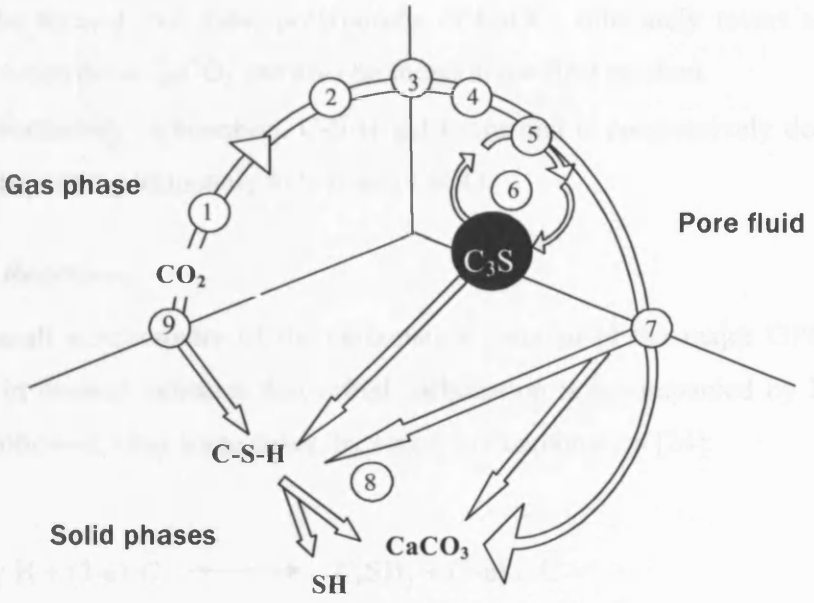

Figure 2-3 Proposed mechanism for accelerated carbonation. Adapted from [38]

The individual steps in the sequence are [38]:

1st. Diffusion of CO_2 in air

2nd. Permeation of CO_2 through the solid

3rd. Solvation of $CO_{2(g)}$ to $CO_{2(aq)}$. Boundary layer transfer is favoured by a high internal surface area of solid.

4th. Hydration of $CO_{2(aq)}$ to H_2CO_3. This is a slow, rate-determining step.

5th. Ionisation of H_2CO_3 to H^+, HCO_3^-, CO_3^{2-}. This occurs almost instantaneously, making the pH fall by approximately 3 units, typically from 13 to 9.

6th. Dissolution of cementitious phases C_3S and C_2S. Because the process is cyclic, this step is rapid and extensive and generates a considerable exotherm. The calcium silicate grains are covered by a loose layer of calcium silicate hydrate gel, which is quickly dissolved, releasing Ca^{2+} and SiO_4^{4-} ions.

7th. Nucleation of $CaCO_3$, C-S-H. The nucleation is favoured by slightly high temperatures and the presence of finely divided material, which acts like heterogeneous nuclei.

8th. Precipitation of solid phases. At the beginning vaterite and aragonite can be formed, but these polymorphs of $CaCO_3$ ultimately revert to calcite. Amorphous $CaCO_3$ can also be found in the final product.

9th. Secondary carbonation. C-S-H gel forms and is progressively decalcified, converting ultimately to S-H and $CaCO_3$.

2.3.3 Reactions

The overall stoichometry of the carbonation reaction of the major OPC silicate phases in cement indicates that initial carbonation is accompanied by hydration and is followed, after some delay, by secondary carbonation [24]:

$$\begin{array}{l} C_3S + y\,H + (3\text{-}a)\,\overline{C} \longrightarrow C_aSH_y + (3\text{-}a)\,C\overline{C} \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad \vdots \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad +b\,\overline{C} \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad \longrightarrow C_{(a\text{-}b)}SH_y + b\,C\overline{C} \end{array} \qquad (2.1)$$

The mechanism of reaction proposed above is based on the knowledge of the behaviour of C_3S during normal hydration. C_2S reacts similarly. First, CO_2 dissolves in water to form carbonic acid. This reaction involves the evolution of considerable quantities of heat, 669.9×10^3 J/mol [19]:

$$\overline{C} + H \longrightarrow \overline{C}H_2 \qquad (2.2)$$

The carbonic acid promotes a vigorous reaction of C_3S in the first 3 minutes [22]:

$$C_3S + 1{,}2\,H\overline{C} \longrightarrow C_{1{,}4}SH_{0{,}6} + 1{,}2C\overline{C} + 0{,}6\,H \qquad (2.3)$$

C_2S reacts similarly. The formation of crystalline $CaCO_3$ is also an exothermic reaction which releases 1205.8×10^3 J/mol [19].

After 3 minutes, carbonation of the gel is the major reaction, implying a change in composition [22].

$$C_aSH_y + (a\text{-}a')\,\overline{C} \longrightarrow C_{a'}SH_{y'} + (a\text{-}a')C\overline{C} + (y\text{-}y')\,H \qquad (2.4)$$

After that, further carbonation occurs, changing the composition of the gel.

The C-S-H is completely decalcified and finally transformed into $CaCO_3$ and highly polymerised silica gel. This gel is acid stable and maintains a similar morphology to the original hydrate [39]:

$$C_3S_2H_2 + 3\,\overline{C} \longrightarrow SiO_{2\,(gel)} + 3\,C\overline{C} + 3\,H \qquad (2.5)$$

2.3.4 Variables Influencing the Carbonation Process

The extent and quality of carbonation, as well as the fixation and immobilisation of specific contaminants, depend upon several parameters. The main ones are the diffusivity and reactivity of CO_2. The following is a scheme of what these factors depend on:

- Carbonation
  - CO_2 Reactivity
    - Solid composition
    - Degree of hydration
  - CO_2 Diffusivity
    - Pore system
      - Characteristics of the solid
      - Water/Solid ratio
      - Degree of hydration
    - Exposure condition
      - CO_2 partial pressure
      - Relative humidity

2.3.4.1 Reactivity of CO_2

For CO_2 to be reactive in order to achieve an effective carbonation, the solid must have certain chemical properties, which are shown in Table 2-3.

Property	Requirement
Solid composition	Materials must be inorganic in nature, containing calcium and/or silicon salts. They may be hydraulic, pozzolanic, lime-bearing, or other CO_2-reactive calcium containing material heavy metals.
pH	The alkaline environment of the solid causes metal hydroxides to form carbonates in the presence of CO_2.
Ca content	Carbonation is known to occur in materials which have available Ca. The higher the concentration of Ca in the material, the better the result of carbonation [40].
Ca/Si ratio	The higher the ratio, the higher the degree of carbonation [41].
Ferrite/C_3A	The presence of these phases are important to the formation of ettringite, which in the presence of CO_2 decomposes to form gypsum, $CaCO_3$ and alumina gel [24].
Organics and anions	The carbonation is affected by their presence in the solid [24].
Certain heavy metals (Pb, Cd, and Ni)	Increase the susceptibility of cementitious materials to carbonation.
Free water content	Materials with high initial free water contents have increased gas permeability, letting more CO_2 enter the solid. There is a lower strength development though.
Microstructure	Higher microporosity of the hydration products, leads to a better carbonated material.
Specific surface area	Materials with lower surface area have lower optimum water-to-solid ratio and vice versa [42].
Permeability	When the gas-permeability of the cementitious material is high, CO_2 penetration is enhanced facilitating carbonation.

Table 2-3 Chemical properties required for effective carbonation

The following is an explanation of how the amount and composition of the reactants (solid, water and CO_2) affect the reactivity of the system.

Solid composition: The existence of certain cementitious phases and specific metals in the waste might influence the rate of the carbonation reaction and therefore, the amount of $CaCO_3$ formed [24]. Some metals, such as Pb, Cd, Ni, can cause an increase in permeability and pore size distribution, causing a decrease of the alkaline buffering capacity of the cementitious solid, a degree of decalcification of the anhydrous calcium silicate phases and an acceleration of hydration. Experimental studies have shown that the amount of $CaCO_3$ deposited in carbonated metal-doped solid can be up to 40% higher than in samples that have not been doped [20].

There are also constituents that influence the carbonation negatively, such as organics and anions, which can react and affect the effective diffusion coefficient of CO_2. The composition of the solid phase can give an idea of the extent of carbonation that can be achieved [43].

Water content: Water is necessary to promote the reaction of CO_2, but too much water limits the reaction due to the blockage of the pores in the solid. The water takes part in the solvation and hydration of the CO_2. It dissolves the Ca^{2+} ions from the solid that will react to form the $CaCO_3$. Therefore, it influences the amount of product generated, which is also related to the strength development.

Electrochemical investigations and studies by x-ray methods have shown that at high water-to-cement ratios (w/c) ranging between 2 and 4, the acidity and resistance of the solution increase sharply after admission of CO_2, which is evidence of effective penetration of CO_2 into such pastes (see Figure 2-4). However, strong materials cannot be obtained at high w/c ratios. At w/c ratios from 0.28 to 0.4, CO_2 does not diffuse into the depth of the material. At low w/c ratios, the gas permeability is increased and the CO_2 effectively diffuses into the material. Hence, the optimum ratio has been found to be between w/c 0.06 and 0.20 [23, 44, 45]. Over w/c 0.25 the reaction is effectively slowed down and the CO_2 uptake is low, although some authors reported to have successfully carbonated with values up to 0.35 [39]. Other authors also showed that different water contents (in some cases higher than 0.2) are required for different cement types in order to achieve the same degree of carbonation [24].

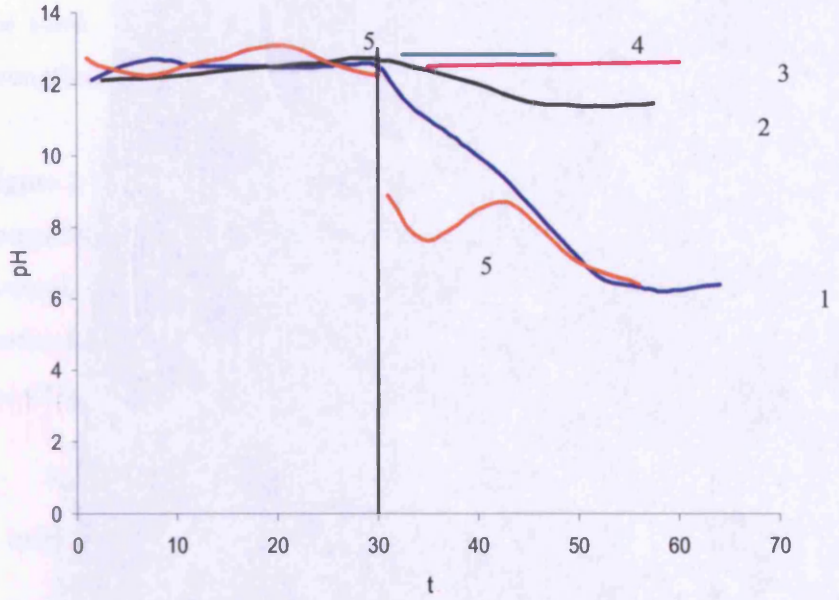

Figure 2-4 Curves for the course of variation of hydrogen-ion concentration (pH) in a CO_2 atmosphere at various water-cement ratios. w/c ratio: (1) 4.0; (2) 2.0; (3) 0.4; (4) 0.28; (5) 0.12. Adapted from [23]

2.3.4.2 CO_2 Diffusivity

Diffusity of CO_2 is constrained by physical properties of the solid. Table 2-4 shows the major physical properties affecting carbonation.

Feature	Effect on carbonation
Size	Finer powders generally show greater degree of carbonation at higher water contents, since there are more surfaces to react with CO_2. Nevertheless, when there are differences in the degree of carbonation between the distinct size fractions of the same material, it could be due to their different compositions. Smaller size fractions carbonate better because they tend to be higher in CaO [46].
Surface area	The higher it is the greater is the extent of the carbonation reaction.
Porosity	Low porosity impedes CO_2 diffusion between particles [40, 47] and is often related to high degrees of compaction.
Permeability to CO_2	Affects the diffusion of CO_2 inside the material and the solubility of phases. Materials with high free water content have lower strength and higher permeability.

Table 2-4 Physical characteristics of the solid influencing carbonation

Compaction pressure

When carbonation is applied to compacted materials, the forming compaction pressure of the granular/powdered material prior to carbonation also influences the resultant product. The porosity and permeability of the solid decrease when the compactation pressure is increased, which leads to greater strength development. Conversely, the low porosity inhibits the diffusion of the CO_2 into

the solid. Thus, the amount of precipitated $CaCO_3$ is lower, resulting in lower strength development.

Figure 2-5 shows the dependence of the strength of carbonated specimens on the compactation pressure. It can be seen that, for each water-cement ratio the strength (R_c) reaches a maximum, indicating that, for any w/c ratio, there is particular compressive force (P_f) at which the cement grains are better accessed by the CO_2 [23].

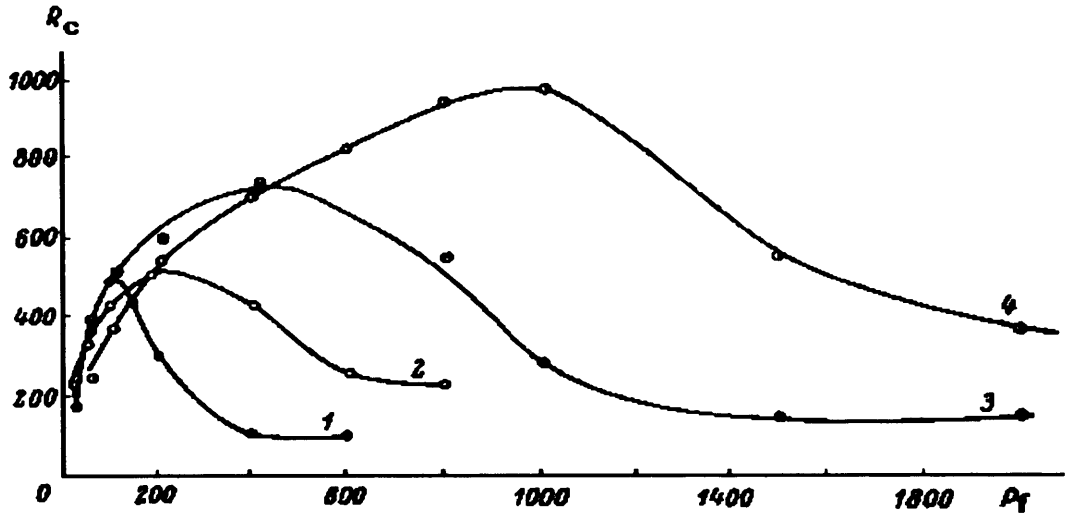

Figure 2-5 Dependence of the strength R_C (kg/cm^2 $\therefore 9.81 \cdot 10^4$ Pa) of carbonated specimens of various w/c ratios on the forming compaction pressure P_f (kg/cm^2). w/c ratio: 1) 0.14; 2) 0.12; 3) 0.1, 4) 0.08. From [23]

Exposure conditions

The system environment also plays a fundamental role in the diffusivity of CO_2. The effect of the main exposure conditions on the carbonation process are shown in Table 2-5.

Conditions	Effect
CO_2 Partial Pressure	The higher the amount of CO_2 in the system, the higher is the rate of the reaction. However, excess CO_2 pressure does not lead to a higher strength of carbonated product [23] (slower reaction would allow for dissipation of heat and reduce stresses in the product). Thus, by varying the partial pressure of CO_2, the rate of carbonation can be controlled and so can the compressive strength [19].
Relative humidity	Carbonation is more rapid at a relative humidity (RH) of 50-60% and decreases at higher and lower relative humidities [17, 48, 49]. As explained before, the diffusion of CO_2 and the reaction kinetics are two conflicting processes, so a compromise in the value of this factor has to be found.
Temperature	The uptake of CO_2 increases with increasing temperature up to 60°C (at atmospheric pressure) [36]. This is most likely due to the leaching of Ca^{2+} ions from the particles of the solid. Higher temperatures decrease the solubility of CO_2 in water, therefore decreasing the rate of carbonation. However, as the carbonation reaction is exothermic, the heat of reaction promotes the formation of meta-stable forms of $CaCO_3$. To obtain the desired stable polymorph (i.e. calcite) the process should be maintained at low temperatures, in the range 0°-10°C. Tests have shown that more calcite is formed if very cold carbonic acid is used for carbonation [50]. Therefore, an optimum for this factor is required.
Pressure	A slight positive pressure of CO_2 increases the rate of reaction and influences the strength development. Carbonation has been carried out at low and high pressures, under vacuum conditions and by supercritical CO_2.

Table 2-5 Effect of the exposure conditions on the carbonation process

2.4 The Results of Carbonation

The results of the carbonation reactions are as follows:

- An acceleration of normal and retarded hydration
- The precipitation of calcite in pore space
- A decalcification of residual cement grains resulting in the selective uptake of certain metallic species
- The precipitation of calcium-metal double salts
- The increased polymerisation of silicate phases
- The formation of metal-silicate complexes

Therefore, the products arising from carbonation induce important physical and chemical changes on the waste material being treated. A detailed explanation of these consequences now follows.

2.4.1 CO_2 Consumption

Pressed ground stainless steel slag, has been found to react readily at low pressure with approximately 18% of its own weight of CO_2 [46]. Other experiments have shown that up to 50 % w/w consumption of CO_2 can be realised following

repeated carbonation steps [32]. Some authors comment that the amount of CO_2 consumed is equivalent to the quantity of calcium hydroxide that is present in the hydrated cement paste [50]. However, they might not be considering C-S-H and aluminate phases, which also can be carbonated.

The theoretical maximum CO_2 uptake capacity upon carbonation can be calculated as a function of the chemical composition of the original material using Stenoir's formula [43] given in equation (2.6). The value calculated gives a measure of the degree to which a material could react. By comparison to the reaction achieved, it can give a measure of the effectiveness of carbonation for the particular solid and conditions used.

$$CO_2\ (\%) = 0.785 \cdot (CaO - 0.7 \cdot SO_3) + 1.09 \cdot Na_2O + 0.93 \cdot K_2O \qquad (2.6)$$

2.4.2 Physical Consequences

One of the main reactions, the carbonation of calcium hydroxide, is accompanied by an increase in solid volume [39]:

$$CH + \overline{C} \longrightarrow C\overline{C} + H \qquad (2.7)$$

Each mole of calcium hydroxide (specific gravity 2.24 g/ml, molar volume 33.0 ml) is converted to the carbonate (specific gravity 2.71 g/ml, molar volume 36.9 ml) with a consequent 11.8% increase in solid volume. The $CaCO_3$ is precipitated in the pore structure of the matrix of the cementitious material and this increase in volume will lead to structural changes. Table 2-6 shows the consequences of carbonation in the solid material.

Characteristic	Consequence
Permeability	It changes due to volume changes and density.
Contaminants	They are absorbed into hydration reaction products, kept insoluble by the high pH environment of the system (typically pH<10) and/or physically encapsulated in the cement matrices. Therefore, metals that could be hazardous, such as Pb, Cd, Mo, Zn, and Ni are converted into their less soluble salts and immobilised [32].
Hydration	It is accelerated. Cementitious compounds considered as poorly hydraulic for practical use, are activated by the CO_2. Carbonation produces carbonate cementation and, as a result, an increase in compressive strength. Materials become less susceptible to shrinkage, and there is an improvement in structural integrity.
Strength	The strength developed in a cement solidified waste cured in a 100% CO_2 atmosphere is 45% higher than that developed when cured in a nitrogen atmosphere. Values of compressive strength up to 7.9 MPa have been found in these systems [51].
Porosity	It tends to drop, as previously large, open pores fill with $CaCO_3$, which has a higher molar volume than the initial calcium hydroxide. Unexpectedly this leads to higher diffusion of the CO_2 [17], perhaps due to shrinkage during carbonation or to variation of the pore system distribution to a larger average pore size.
Tortuosity	In hydrated products it is higher than in a non-carbonated solid, so carbonation may lead to more rapid leaching of some species.
Pore size distribution	A carbonated material can have approximately twice as much volume attributed to small pores as a non-carbonated one. The precipitated $CaCO_3$ has very low solubility and will therefore block the pore system. However, due to the volume expansion involved in the reaction there will be microcracks in the carbonated zone [42].

Table 2-6 Variations in certain physical properties due to carbonation

Figure 2-6 shows how the pore volume of the carbonated sample (b) is lower than the non-carbonated sample (a). Studies using image analysis on cement stabilised wastes have shown a decrease of up to 26% in the observable pore volume [41].

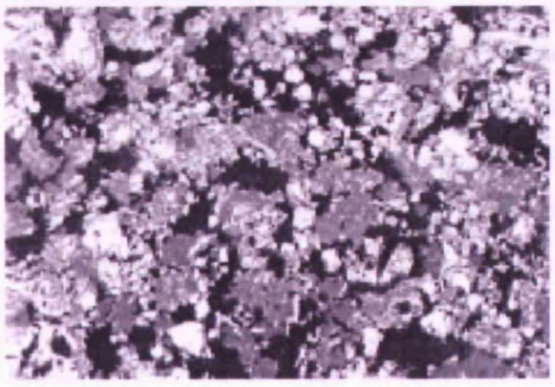

Figure 2-6 (a) General view of non-carbonated sample [41]

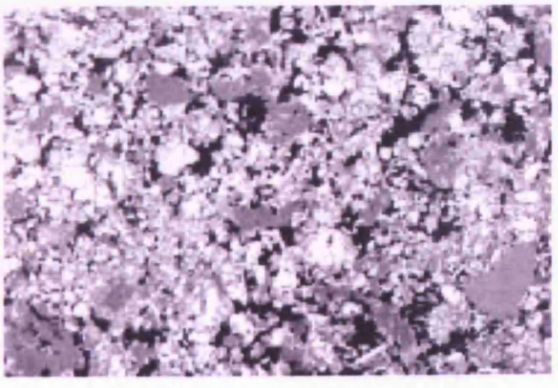

Figure 2-6 (b) General view of carbonated sample [41]

2.4.3 Microstructural Changes

Portlandite is arranged in a crystalline structure, which is assumed to be intimately intergrown with the C-S-H [52]. The microstructure is characterized by the

precipitation of calcite in the pores, the decalcified C-S-H gel, and the production of gypsum from the decomposition of ettringite.

During carbonation, the three polymorphs of $CaCO_3$ may be produced. The morphology of calcite is characterised by small, tightly packed crystals (<3μm) of acicular shape. Some microcracking is also noticeable [51], caused by the volume expansion during the reaction [42], although Lange et al. state that this is the result of thermal stresses caused by heat generated during carbonation [51].

The C-S-H is converted into silica gel by the reaction with CO_2. This gel has an unbranched polymeric structure, and by means of carbonation, polymerization is promoted with a structural rearrangement [39], leading to a silica framework dominated structure.

After carbonation, a calcite rich matrix filling the pores of the system can be observed when analysing wastes containing heavy metals. The residual non-carbonated grains are enveloped by a silica-rich decalcified rim which also encapsulates heavy metals such as Pb and Zn. Other metals such as Ni and Cr appear to be immobilised in the calcite-filled porosity [51].

2.4.4 Chemical Consequences

With progressive carbonation, the pH of the system gradually drops by around 3 units, leading to altered solubility (sometimes lower, sometimes higher) of contaminant metals previously immobilised by the high pH of the wasteform [17]. The decrease in pH due to carbonation is dependent on the relation between the rate of dissolution of the solid calcium hydroxide through the following equation:

$$CH_{(s)} \longrightarrow Ca^{2+}{}_{(aq)} + 2\,OH^{-} \qquad (2.8)$$

and the rate of consumption of OH^{-} in the carbonation process. When the solid portlandite is consumed, the process becomes diffusion controlled, so the dissolution rate becomes slower. Consequently, a high concentration of hydroxide ions in the pore solution cannot be maintained when carbonation takes place [42].

There is also a change in the redox conditions. Carbonated systems are mildly reducing.

The ANC for carbonated systems increases under acidic conditions. Experimental work on carbonated MSWI BA has demonstrated that at pH 5, the ANC can double, reaching a value of 0.88 meq/g after 48 hours of accelerated carbonation [53].

Heavy metal immobilisation in carbonated systems can be related to either physical containment, or chemical fixation. The lower solubility of heavy metals in the alkaline pore solution explains the chemical fixation of heavy metals.

Alternatively, the major anions (i.e. nitrate, sulphate, chloride, fluoride) are usually incorporated in the lattice or in the interlayer regions of the hydration products. These products have low solubility at high pH conditions, but are unstable at the pH produced by the carbonation reaction (pH = 7 – 8.5) and dissolve, releasing their entrained anions. These anions will finally precipitate as salts which are readily leached by water [15].

2.4.5 Leaching Behaviour

Due to changes in the microstructure, pH, and redox conditions, there is a selective release of specific waste components (as in non-carbonated products). The effect of carbonation is twofold: some heavy metals form either hydroxi-carbonate or carbonate and deposit on the calcium silicates. Furthermore, for many metals the decrease in the pH reduces metal mobility, whilst for others there is an inversely proportional relationship between the pH and the leaching rate. For certain species, there is a stabilisation of metal carbonate precipitates, due to the provision of CO_2, whilst at the same time there is an increase in the leaching rate due to the lowering of the pH.

Table 2-7 gives a summary of the behaviour of various species that can be present in the leachate of a carbonated solidified waste form. The leaching behaviour in hydrated and non-hydrated mixtures is differentiated, as they can perform in different ways.

Species	Behaviour
Cu	**In hydrated systems** Carbonation in most cases increases Cu leachability due to (a) an increase in the solubility of the metal compounds through the reduction of the pH, (b) the decomposition of ettringite ($C_6A\hat{S}_3H_{32}$) and (c) the polymerisation of the C-S-H releasing metal cations that were linked to the Si-O groups [14]. In other cases lower leachability has been reported [54]. **In non-hydrated systems** Cu is well retained [51]. However, in some cases a higher leaching after carbonation has been observed, identifying $Cu_2(OH)_2CO_3$ as a possible solubility-controlling solid [55].
Zn, Pb	**In hydrated systems** They are moderately mobilised due to the lowering of the pH, although their concentration in the leachates is below the regulation limits [18, 20]. These metals form either hydroxi-carbonates or carbonates that deposit on the calcium silicate minerals [14, 20]. In comparison with other metals, they are the best retained species. Decreased leaching has even been reported for Pb due to the diminished amphoteric behaviour caused by the formation of sparingly soluble $PbCO_3$ [54, 56]. **In non-hydrated systems** The leaching of Pb is markedly decreased by carbonation as it is involved in sorption phenomena onto neoformed minerals [35, 55].On the other hand, Zn has shown positive results in some cases [35], while in others the leaching is increased due to the dissolution of carbonate minerals at acidic pHs [55].
Mn	The leaching of this metal is increased by carbonation [14].
Ni, Cd, Co	**In hydrated systems** These metals are mobilized due to the low pH of the system. Cd forms carbonates and hydroxicarbonates [18, 20, 56]. Ni and Co can replace Ca in calcium silicate hydrate [18, 20], although some authors have reported positive results for Ni, due to the presence of part of the metal as carbonates [54]. **In non-hydrated systems** Carbonation may increase the leaching of Ni due to the lower pH of the system (pH = 7-8.5), however at a field scale trial it was reduced significantly [35].
Ba	The leaching is much lower in carbonated samples due to its insolubilisation through the formation of $BaCO_3$ and $BaSO_4$, and the decomposition of ettringite [14, 54].
Cr	**In hydrated systems** This metal substitutes for silicon and chemically incorporates into C-S-H [20]. In some cases its leachability is increased by carbonation due to the pH decrease and polymerisation of C-S-H, but its concentration is below the set limits [5]. **In non-hydrated systems** Leaching has been seen to decrease as a result of the formation of calcite, the modification of the pore structure and the precipitation of double salts containing toxic species due to the high affinity of its oxyanions with respect to the neoformed minerals [31, 55].
Hg	Hg remains as an oxide, so it is not well retained [20]. HgO does not react with cement.
Sr	The leaching of this element is diminished by carbonation. The metal is more tightly bound through solid solution in $CaCO_3$ [18].
As	This metal is not well retained in carbonated samples, unless pre-treated first [15, 56].
NO_3^-	These ions are rapidly released, revealing the physical changes occurring in the carbonated waste form [15, 18].
Cl^-	These ions are only partially immobilised, mainly due to the decomposition of Friedel's salt [5, 14, 15].
SO_4^{2-}	Their concentration in the leachates is below the limits, even though their leaching is increased due to the decomposition of ettringite [5, 15].

Table 2-7 Leaching behaviour of different species due to carbonation

2.5 Process Methods

Different methods of applying carbonation are possible including the use of increased pressure, both in the presence and absence of steam, vacuum de-airing, use of low water contents, and compactation of samples prior to carbonation. Hitherto, technical limitations and high costs have prevented commercial development. The main factor that has lead to the search for alternatives routes to carbonate cementitious materials is the dependence of the reaction on the content

of water in the system so that there is enough water for the reaction without blocking the pores of the solid. Table 2-8 shows some of the methods of carbonation.

Method	Main feature
Carbonation with dry CO_2 under pressure	The solid samples are dehydrated by the flowing of the dry gas, causing water starvation in the carbonation reaction.
Carbonation in static and dynamic systems at low pressures	The heat released by the reaction vaporizes a portion of the water present within the solid. In the dynamic system, the constant flow of CO_2 helps to remove this water vapour, while in the static system, the water vapour is trapped and can saturate the CO_2 atmosphere [19]. In addition, diffusion is facilitated when carbonating in dynamic conditions.
Vacuum carbonation	This is carried out at near vacuum pressures in the presence of a desiccant [15].These conditions diminish the resistance of water transport from the carbonating solid to the desiccant due to the large average free space left for the water vapour molecules. This method has been shown to give more complete carbonation.
Carbonation at high pressure	At elevated pressures, larger amounts of gas are introduced throughout the sample before pore closure occurs, so carbonation is enhanced [19].
Supercritical carbonation	The gas in these conditions increases the reactive inner surface of the cementitious solid microstructure, by dissolving the pore water content and replacing the structurally bound water of $Ca(OH)_2$ and C-S-H with CO_2 [57]. The $scCO_2$ behaves like a dense gas, acting as a solvent for water [57], but no surface tension, allowing penetration into very fine pores. The result is a product with enhanced mechanical properties, and a considerable morphological change [58].

Table 2-8 Methods of carbonation and their main features

When carbonation is carried out under pressure in a static system, the penetration of CO_2 into the sample controls the reaction rate, due to the lower vaporization of the water in the sample. At elevated pressures, larger amounts of gas are introduced throughout the sample before pore closure occurs, so carbonation is enhanced [19]. If the carbonation is attempted with dry CO_2, a water starvation results, which impedes carbonation.

In a dynamic system the reactivity of cementitious materials is enhanced, leading to a higher amount of carbonation achieved even at low pressures, whilst in static systems at low pressures the water vapour is trapped and saturates the CO_2 atmosphere. On the other hand, if the reaction is completed at near vacuum conditions with the help of a desiccant, the water generated during the reaction maintains an open pore network. Only carbonation at near atmospheric pressures (1-5 bars) is considered here for practical, cost-effective applications.

2.5.1 Process Scale-up

Accelerated carbonation is a technique with great potential to be industrialised. Figure 2-7 shows the experimental batch process applied in the first pilot-scale trial carried out in Dartford, Kent. It shows separate mixing and carbonation chambers, whereas a combined mixer and carbonation process is currently being used. This scheme has been further developed, and is now available as a continuous process capable of a 50t/hour throughput [59].

Other authors have considered the possibility of carrying out *direct carbonation* in a rotary kiln type operation, or a fluidised bed process. Process heat integration is required so that there is heat exchange between the hot reaction products and the cold reactants. This is considered to be the best method if the raw materials react quickly with CO_2 at elevated temperature. Costs will be seriously affected if high pressures are required in the operation [60].

Figure 2-7 Schematic of an accelerated carbonation process (courtesy of Forkers)

2.6 Conclusions

The effects of carbonation on the properties of cementitious materials depend on the nature of the material. Despite the known adverse effect in some systems, in many cases the outcomes may be beneficial.

- There is great potential to apply carbonation technology, not only to the stabilisation of a vast range of waste materials but also to the generation of products with specific physical and chemical properties.
- To be susceptible to carbonation the materials must be inorganic in nature, containing calcium and/or silicon salts. They may be hydraulic, pozzolanic, lime-bearing, or other CO_2-reactive calcium-containing material with heavy metals.
- Greater carbonation is achieved when the solid has high concentration of CaO, and presents a high surface area. As regard the exposure conditions, the carbonation is optimum when the relative humidity is kept at 60-70% and the pressure is slightly positive.
- After the treatment, the contaminants, namely heavy metals, are either absorbed, or insolubilised, or physically encapsulated. Carbonation could have either a beneficial or deleterious effect on (trace) element mobility in cement-based systems, which seems dependent on the type of waste and the type and severity of the CO_2 treatment.
- The strength developed in a carbonated solid can be up to 45% higher than that developed when cured in nitrogen atmosphere.
- Some waste materials have consumed more than 50% CO_2 w/w, which indicates the great potential for the utilisation of CO_2 emissions.

There is a growing interest in the potential of accelerated carbonation technology because it has been demonstrated that contaminated solids of cementitious nature can be rapidly remediated whilst binding significant quantities of CO_2. Therefore, accelerated carbonation provides a way of sequestering CO_2 as a solid salt in a variety of treated products reducing landfill waste volumes.

CHAPTER 3

3 Waste Material Selection

3.1 Selection of Material

Carbonation is known to affect a wide range of calcium and magnesium-based materials (see Table 2-1). As a result of the reaction, chemical (see section 2.4.4) as well as physical properties (see section 2.4.2) are improved to an extent that might make them meet the requirements to be used as engineering fill.

A review has been carried out to identify the most economically viable waste for accelerated carbonation treatment, in terms of the impact on current waste management practices and in meeting the challenges set by recent legislation [61]. The European Waste Catalogue (EWC) [62] has been the selected starting point for this review. The index of the hazardous list in the EWC is reported in Table 3-1.

Through a first screening step, only UK thermal residues have been considered, given that combustion processes are commonly used in waste management to minimise waste volumes and eliminate organic compounds which affect carbonation negatively [43]. Thus, inorganic wastes from thermal processes and wastes from central treatment facilities, off-site wastewater treatment plants and the water industry, identified by indexes 10 00 00 and 19 00 00 respectively in the list, have been chosen for investigation. For those, available data have been collected from the Environmental Agency. The total amount of wastes produced per year, in England and Wales, together with land disposal options and the amount reused and recycled have been obtained and are reported in Appendix 1.

Catalogue no.	Waste
01 00 00	Waste resulting from exploration, mining, dressing and further treatment of minerals and quarrying
02 00 00	Waste from agricultural, horticultural, hunting, fishing and aquaculture primary production, food preparation and processing
03 00 00	Wastes from wood processing and the production of paper, cardboard, pulp, panels and furniture
04 00 00	Wastes from leather and textile industries
05 00 00	Wastes from petroleum refining, natural gas purification and pyrolytic treatment of coal
06 00 00	Wastes from inorganic chemical processes
07 00 00	Wastes from organic chemical processes
08 00 00	Wastes from the manufacture , formulation, supply and use (MFSU) of coatings, (paints, varnishes and vitreous enamels), adhesives, sealants and printing inks
09 00 00	Wastes from the photographic industry
10 00 00	Inorganic wastes from thermal processes
11 00 00	Inorganic waste with metals from metal treatment and the coating of metals, non-ferrous hydrometallurgy
12 00 00	Wastes from shaping and surface treatment of metals and plastics
13 00 00	Oil waste (except edible oils, 05 00 00 and 12 00 00)
14 00 00	Wastes from organic substances employed as solvents (except 07 00 00 and 08 00 00)
15 00 00	Packaging, absorbents, wiping cloths, filter materials and protective clothing not otherwise specified
16 00 00	Waste not otherwise specified in the catalogue
17 00 00	Construction and demolition waste (including road construction)
18 00 00	Wastes from human or animal health care and/or related research (excluding kitchen and restaurant wastes which do not arise from immediate health care)
19 00 00	Wastes from treatment facilities, off-site waste water treatment plants and the water industry
20 00 00	Municipal wastes and similar commercial, industrial and institutional wastes including separately collected fractions.

Table 3-1 European Waste Catalogue

A systematic evaluation, based on available data, has been carried out, considering the UK waste streams that produce the largest amounts of residues, in order to increase the likely impact of the research and to improve the chance for any new products being created to be economically viable.

As a first screening step, wastes not suitable for treatment through accelerated carbonation were eliminated from further consideration. They were selected on the basis of technical experience on the constitution of the materials, or the amount produced in the UK.

A subset of waste materials selected on the basis of their bulk chemistry and their availability, were subjected to accelerated carbonation to ascertain which were most susceptible to the treatment. Table 3-2 shows the chosen materials and their respective bulk compositions [63]. The experiments were carried out at the University of Greenwich by Derek Johnson [40].

Sample	CaO	SiO_2	MgO	Fe_2O_3	Al_2O_3	others
Ordinary Portland Cement (OPC)*	65.04	20.71	1.03	2.77	4.83	4.36
Stainless Steel Slag (SSS)*	46.66	27.92	9.75	1.22	2.91	7.26
Ash from combustion of de-inking sludge from paper recycling*	37.69	33.76	3.72	0.03	20.12	3.52
Pulverised Fly Ash (PFA)*	3.36	46.96	1.76	11.33	23.71	7.22
Blast Furnace Slag (BFS)*	41.38	34.59	6.84	1.51	14.02	1.66
MSWI APCr*	35.89	15.29	1.29	1.11	6.25	13.94
MSWI BA*	22.62	10.32	1.61	0.95	5.30	24.78
Precipitated 1:1 calcium silicate powder (CS)	56.00	44.00	-	-	-	-
Cupola Arrester filter cake	8.00	15.00	2.00	23.00	4.00	49.00
Slag (Sa)	46.00	10.00	3.00	1.00	32.00	9.00
Slag (Sb)	11.00	40.00	35.00	1.00	8.00	6.00
Cyclone Dust	6.00	30.00	1.00	39.00	6.00	2.00
Cupola Furnace Dust	25.00	30.00	1.00	23.00	4.00	18.00
Slag (Sc)	37.00	41.00	2.00	1.00	12.00	9.00

Table 3-2 Composition of wastes in percentage by weight. (*after [40])

Carbonation was carried out in a stainless steel sample chamber, exposing the wastes to a 100% CO_2 atmosphere at 65% relative humidity and at a pressure of 3 bars for 24 hours. Prior to the reaction the dry powder was mixed with a known amount of water and after 24 hours exposure the samples were dried at 60°C to constant weight. The gain in weight experienced by the different wastes is proportional to the CO_2 that has reacted with the sample [40].

Figure 3-1 shows the gain in weight of the samples against the calcium oxide composition of the initial waste. The degree of carbonation is strongly dependent upon the calcium content and a clear trend is easily observable. However, some wastes do not seem to follow this tendency. This could be due to lack of calcium hydroxide and/or the presence of certain components that might influence the effective diffusivity and reactivity of the CO_2. For example, the slow hydration of GGBS, which facilitates CO_2 diffusion, is due to the breakdown of the glassy structure of the slag in alkaline conditions. Therefore, the absence of alkaline conditions may hinder the accelerated carbonation of this material.

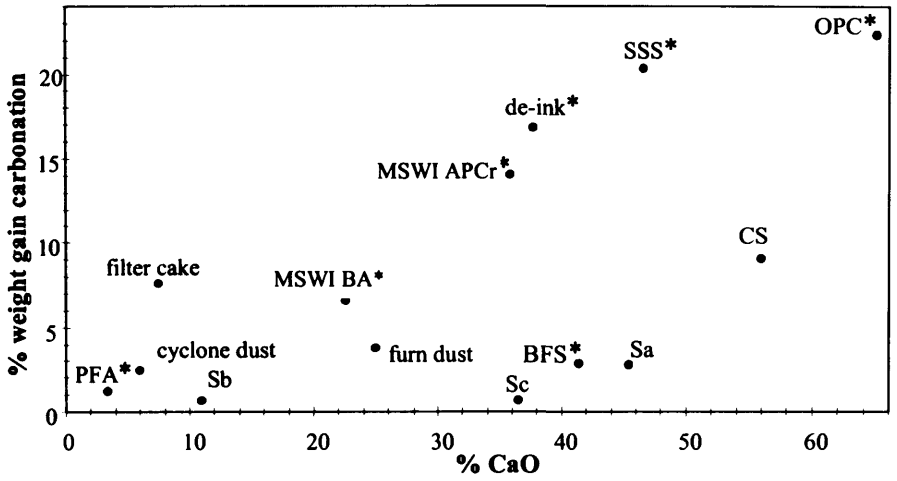

Figure 3-1 Percentage of weight gain upon carbonation for weight percentage of free lime of waste. (*after [40])

The second screening step involved considering the following factors:

- the results of the experimental study
- the total amount of wastes produced per year
- the land disposal options
- the amount reused and recycled

On this basis, PFA, BFS and MSWI APCr were short-listed for closer analysis (see Table 3-3). These three wastes are produced in large quantities in the UK. PFA and MSWI APCr are mainly disposed of in landfill sites, whereas a considerable fraction of BFS is recycled.

Catalogue no.	Name	Landfill	Recycling Reuse	Waste transfer	Treatment	Total
10 01 01	PFA	3,100,000	2,000,000			5,100,000
10 09 03	BFS	1,000,000	3,000,000			4,000,000
19 01 03	MSWI APCr	73,920		149	9,931	84,000

Table 3-3 Chosen UK wastes from thermal processes. Amounts in tonnes/yr [61]

In Table 3-3 'Waste Transfer' refers to wastes that do not go directly to final disposal, treatment or recovery. These wastes normally go through a transfer process and may be "bulked-up" prior to recycling, treatment or ultimate disposal. 'Treatment' refers to all physico-chemical treatment.

3.1.1 Blast Furnace Slag

Furnace slag is a by-product of the iron and steel industry. The ore, iron scrap, limestone dolomite and coke are the feedstock for iron and steel production. These materials are charged in a blast furnace (Figure 3-2) and the outlet of the process is a molten iron product and furnace slag. The residues are glassy and typically contain silica, alumina and CaO.

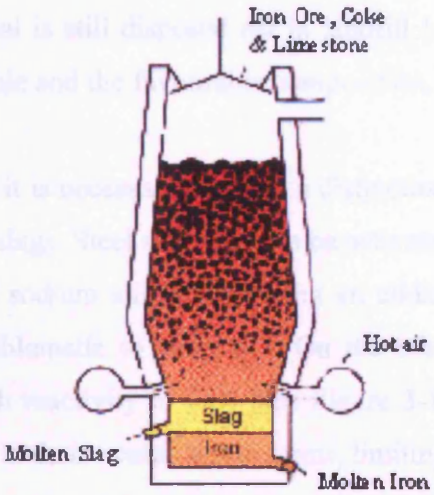

Figure 3-2 General schematic of a blast furnace [64]

The physical properties of furnace slag are strictly related to the production process. Depending on its management, furnace slag is classified as *air-cooled blast furnace slag*, *expanded slag*, *granulated blast furnace slag* and *pelletized slag* (which is the most common furnace slag).

Air-cooled slag is obtained by slowly cooling the molten slag under ambient conditions so that it crystallises into a dense product. Because of its mechanical properties, air-cooled blast furnace slag is commonly used as an aggregate in asphalt paving and granular-base applications [65]. Expanded slag is the least commonly produced, but is recognisable by its relatively high porosity and low

bulk density resulting from its faster solidification involving controlled quantities of water, air, or steam.

Pelletised slag is obtained when air and water are used to quench liquid slag. In this case, the amount of glass depends on the speed of the cooling process. In particular, when cooling involves water quenching, it is so rapid that a vitrified, granulated slag is obtained. The cementitious properties of this slag are used to produce blended cement. In particular, the slag is commonly premixed with Portland cement or hydrated lime.

Furnace slag is widely reused and recycled in the construction industry; however a large amount of material is still disposed off in landfill (see Table 3-3). Despite the high volume available and the favourable composition, BFS has been rejected.

To justify this decision it is necessary to make a distinction between blast furnace slag and stainless steel slags. Steel slags need to be activated for carbonation using sodium hydroxide and sodium silicate implying an additional process step that could be costly or problematic to carry out. On the other hand, stainless steel slags, despite their high reactivity to CO_2 (see Figure 3-1), may not sufficiently immobilise Cr^{6+} and F^- in their treated waste forms, limiting its re-use [55].

Therefore, BFS has been disregarded for an economically viable carbonation process due to previous experience carbonating this residue. It may however be economical to carbonate blast furnace slag when blended with other waste materials.

3.1.2 Pulverised Fly Ash

Power station ash is a by-product of the use of coal for the generation of electricity. In the UK, coal fired power stations burn bituminous or hard coals and a small amount of anthracite. The pulverised coal is burned within 3-4 seconds in a furnace at around 1400°C. Some solid particles are carried away by the flue gas and are melted, forming spherical shapes. Because of the rapid cooling they solidify as an amorphous glassy material. These solid particles are then

transported with flue gas through the boiler, where they are captured in electrostatic precipitators and classified as pulverised fly ash (PFA).

PFA can be withdrawn as a dry product, or can be conditioned by mixing with water to make it easier to transport or store. The sphericity and the particle distribution make the PFA a good choice for reuse in construction material.

PFA is composed of silica, alumina and iron oxides, which account for 75-85% of the materials composition and less than 5% of CaO (see Table 3-2). It is a pozzolanic material, forming stable cementitious compounds in the presence of lime and water. This characteristic encourages its reuse in the construction industry.

Even though a high amount of power station ash is presently not recycled (see Table 3-3), the low calcium content suggests that the potential for carbonation of UK PFA on its own is low.

3.1.3 MSW Incinerator Residues

29.1 million tonnes of MSW were produced in England in 2003/2004 [66]. The common disposal methods for MSW are: landfilling, recycling or composting and thermal treatment. In 2003/04, 27.9% (8.1 million tonnes) of MSW were recovered either through recycling, composting, or extracting energy from waste. This amount has been steadily increasing over the last few years (it was 18% in 1999/02), however, it is still far from the target of 40% set by the Waste Strategy 2000 for England and Wales for the management of municipal and household waste [66].

The amount of waste sent to landfill has decreased over the last few years but it is still the most significant fraction, 72% (22.1 million tonnes) in 2003/2004. The proportion of household waste recycled (including composting) is 17.7% whilst the amount of MSW sent to thermal treatments is 10.2% [66].

Bio-treatment, by anaerobic digestion, is only effective for the putrescible part of the waste. Landfill of MSW generates methane, a greenhouse gas with global

warming potential[3] 20 times higher than CO_2. Thermo-treatment methods include incineration, gasification and pyrolysis. Gasification and pyrolysis are thermal reactions carried out to less than full oxidation by restricting the available oxygen. There are no commercial facilities in the UK for either the pyrolysis or gasification of MSW.

Incineration is the combustion of waste in excess of oxygen. In an incinerator the unprocessed MSW is burnt at 700°-1000°C, resulting in CO_2, water vapour and a solid residue which generally accounts for 30-35 wt. % of the burnt waste and 10% of the initial volume. The solid residue is made up of two streams, BA and APCr. The latter are usually contaminated with heavy metals and are consequently difficult to dispose of. The composition of these ashes depends on the waste input, which varies with the location, season, local recycling schemes, etc.

It is known that is possible to use these ashes as a substitute for fine aggregates for construction purposes, especially BA (reuse of APCr is hindered due to high chloride content). In fact, the alarming decrease in primary aggregate resources has led to recent legislation to encourage the development of alternative sources [68]. Before reusing these ashes a stabilization step is required. The general trend is to leave them in open storage piles for three months so that they stabilise naturally. As a result, the ashes modify their pH, redox potential, leaching behaviour, as well as ANC.

In many cases the re-use of MSW ashes as aggregate materials has failed due to cracking, lack of strength and specially due to leaching problems. One way in which these properties can be improved is by using accelerated carbonation. Carbonation is one of the reactions involved in the weathering stage, thus through accelerated carbonation this reaction can be enhanced, speeded up and controlled, giving as a result a stabilised solid with improved properties and greater potential to be engineered.

[3] Global Warming Potential (GWP) is a measure of how much given mass of greenhouse gas is estimated to contribute to global warming. It is a relative scale which compares the gas in question to that of the same mass of CO_2 whose GWP is one [67].

The chemical and physical properties of MSWIr make them optimum for accelerated carbonation. They are rich in calcium oxide and silica, particle size matches the required dimensions for aggregates and the high superficial surface area also favours the reaction. Hence, basing on volumes produced current disposal routes and physical and chemical characterisation, MSWIr have been selected as the most suitable waste for accelerated carbonation application.

3.2 MSW Incinerator Residues

3.2.1 MSW Incineration

Incineration is the combustion of waste in the excess of oxygen. The hot air goes through the boiler to produce high-pressure steam and then to a turbine to generate electricity. After incineration the wastes are converted to CO_2, water vapour and ash.

Figure 3-3 Typical schematic of incinerator (SELCHP incinerator)

Figure 3-3 shows a diagram of a typical MSW incinerator (South East London Combined Heat and Power (SELCHP)). Waste collection lorries drive into a waste reception building (1) and empty MSW into special reception bays (2). The mixed waste is then taken from these bays by overhead cranes (3) and fed (4) into the combustion chambers (6 and 9). Fans (7) draw or force air through the waste

and into the combustion chamber. The waste ignites as it enters the combustion chamber. This typically operates at a temperature of 850 °C. A moving grate (6) transfers the burning waste along the combustion chamber. As the waste burns, it produces hot gases and ashes. The flue gas is emitted to the air after the gas treatment process.

The hot ashes either fall through or off the end of the grate into a quenching pit (20) to cool down. The drained ashes are then passed under electro-magnets (19) to recover metals for recycling. The recovered fraction is around 1% to 1.5% by weight. The remaining ash is known as BA and is generally sent to landfill or for processing. BA represents approximately 25% to 30% by weight and 10% by volume of the input to the incinerator. Figure 3-4 shows the wet BA stored at the SELCHP incinerator prior to disposal.

Figure 3-4 Quenched BA stockpiled prior to disposal (SELCHP incinerator).

The hot gases carrying fine particles of ash circulate through the boiler (9) generating high pressure steam. This steam gives power to several turbines coupled to generators (15), supplying electricity to the National Grid. The hot water from the turbines is cooled prior to being reused (16). Some of the fine ash particles are deposited on the boiler tubes and fall back onto the grate.

The combustion gases have low pH due to the presence of chlorine and sulphur and they also contain dioxins and high concentrations of fine particles (fly ash). To purify the gases lime is added to neutralise any excess acid (12), fine carbon is added to remove dioxins and heavy metals, and finally the fly ash, carbon and lime are removed by bag filters (13). Table 3-4 shows MSW incineration emissions in the UK, during 1990 and 1998.

Contaminant	Emissions 1990	Emissions 1998
CO_2	217.50	186.30
CO	2.04	0.40
SO_2	3.94	0.15
NO_x	5.21	5.21
particles	0.86	0.06
As	1.09	0.70
Cd	7.18	0.09
Cr	12.96	0.24
Cu	17.90	0.58
Hg	5.07	0.31
Ni	7.82	0.28
Pb	130.50	0.28
Zn	215.40	6.78

Table 3-4 MSW incineration emissions in the UK, 1990 and 1998 (tonnes) [69].

The carbon and the fly ash contain most of the dioxins produced in the process. The combined residues from gas cleaning are known as air pollution control residues (APCr). These are sent to special landfill sites or to treatment plants. APCr represent approximately 3% by weight of waste input.

3.2.2 Legislation Affecting MSWIr

In 1999, the EU introduced the Landfill Directive 99/31/EC. This requires the reduction of landfill of biodegradable municipal waste, bans the co-disposal of hazardous and non-hazardous wastes, forces the pre-treatment of hazardous wastes through physical/thermal/chemical or biological process before disposal and restricts the number of landfill sites [4].

In addition, there are further restrictions on landfilling imposed by the Waste Acceptance Criteria for granular waste, which came into force in July 2005. The treatment residues may not be disposed of at a landfill site where the waste

acceptance criteria, based on standard batch leach test[4] (British Standards Institution, 2002) or column test (Comité Européen Normalisation, 2002) results, are exceeded for a particular class of landfill. This means that severe treatment of MSWIr, especially APCr, may be necessary to meet the criteria for a number of metal and anions [12].

The Incineration Directive 2000/76/EC [70] was adopted in December 2000, for implementation by Member States at the end of 2002. The stringent controls on MSW incineration plants are shown in Table 3-5. Subsequently, the reduction of emissions to air has resulted in an increase in the toxic substances left behind in the incinerator ash, especially in the APCr fraction.

Pollutants	**Air emission limit values (mg/m^3)**
Total dust	10
Gaseous and vaporous organic substances	10*
HCl	10
HF	1
SO_2	50
NO and NO_2 expressed as NO_2 for existing incineration plants with a nominal capacity exceeding 6 ton/h or new incineration plants	200
NO and NO_2 expressed as NO_2 for existing incineration plants with a nominal capacity of 6 ton/h or less	400
Cd + Ta	Total 0.05
Hg	0.05
Sb + As + Pb + Cr + Co + Cu + Mn + Ni + Vn	Total 0.5
Dioxins and furans	0.1

*expressed as total organic carbon

Table 3-5 Air emission limit values for incinerators [70]

3.2.3 Incinerators in England and Wales

There are 12 incinerators in England and Wales, which are dealing with ~10% of the 29.1 million tonnes of MSW produced in 2000/01. MSW accounts for around 90% of the waste burned by these incinerators, the rest is non-hazardous commercial and industrial waste. Table 3-6 shows the location, owners and capacity of the 12 incinerators.

[4] The test is designed to examine the short-term and long-term leaching behaviour for landfill. It is two-step leaching test with liquid/solid = 10 L/kg. The ash is leached at L/S=2l/kg for 6 h end-over-end shaking and then filtered. The residues are leached further at L/S = 8 l/kg for 18 h.

Location	Owner	Capacity (t/year)
Bolton	Greater Manchester Waste	120,000
Cleveland	SITA Holdings (UK) Ltd.	220,000
Coventry	Coventry and Solihull Waste Disposal Ltd	260,000
Dudley	MES Environmental Ltd.	90,000
Edmonton	London Waste Ltd.	500,000
Nottingham	Wastenotts (Reclamation) Ltd.	150,000
SE London	South East London Combined Heat and Power Ltd (SELCHP)	420,000
Sheffield	ONYX Sheffield	135,000
Stoke	MES Environmental Ltd	200,000
Tyseley	Tyseley Waste Disposal Ltd	350,000
Wolverhampton	MES Environmental Ltd.	105,000
Huddersfield	SITA Holdings (UK) Ltd.	150,000

Table 3-6 MSW incinerators in England and Wales, 2003 [71]

Between 1996 and 2000, the incinerators reported production of 2.78 million tonnes of BA, about 314,000 tonnes of APCr and 177,000 tonnes of recovered metals [2]. Details of the BA and APCr production of the incinerators in England and Wales in 2000 are given in Table 3-7.

Incinerator	BA	APCr
Bolton	11,904	1,353
Teesside (Cleveland)	7,624	5,848
Coventry	33,148	7,194
Dudley	21,132	4,178
Edmonton	134,570	15,858
Nottingham	37,938	7,859
Lewisham (SE London)	107,923	14,840
Sheffield	39,852	3,333
Stoke on Trent	50,001	6,472
Birmingham	77,054	8,717
Wolverhampton	28,830	4,650
Totals	642,088	79,771

Table 3-7 Summary of BA and APCr production figures (tonnes) [2]

The UK's Environmental Agency believes that incineration has a role in MSW management. They promote the controlled use of incineration under EU regulation and the recovery of energy generated by incineration.

3.2.4 Bottom ash

BA, which constitutes 80% of the incinerator residue, is a heterogeneous mixture of slag, grate sifting, boiler ash, metals, ceramics, glass, other non-combustibles and unburned organics. This ash is classified as a non-hazardous waste according to the European Waste Catalogue and consists mainly of aluminosilicate phases and certain amounts of metallic components (~8%), namely Cr, Ni, Cu, Zn, Ba, Pb, Cd, As, Ti, Mn and Hg.

3.2.5 Air Pollution Control Residues

APCr are a mixture of fly ash, carbon and lime and are the result of the treatment process to clean the gases before they are released into the air. APCr are classified as a hazardous waste due to its strong alkalinity, high content of lime and other calcium compounds, the high concentration of heavy metals and chlorinated compounds, in addition to soluble salts. Moreover, it consists of very fine particles, mostly <300μm in diameter.

3.2.6 MSWIr Treatment and Disposal

In the UK 79% of the BA is sent to landfill sites, whilst the rest goes to waste treatment plants, local engineering departments and trial road making applications. 88% of the APCr are sent to landfill whilst the rest is sent to waste treatment plants.

In the processing plants, BA is first stabilised in stockpiles at landfill sites for 3-6 months to absorb water, reduce alkalinity and make handling easier. It is then screened to separate and remove oversized material. Ferrous and non-ferrous materials are recycled and the ash is finally grated into different sizes according to the intended use. Up to 20% of BA has a particle size > 10cm in diameter. The fraction < 10cm is somewhat uniform, with up to 10% fines < 2cm in diameter. This latter fraction resembles well grated sand and gravel and can be used as lightweight aggregates [72].

The use of processed BA is long-established in several European countries, USA and Japan. However, in the UK the market is still in a very early stage. In the UK,

it has been used as additive for asphalt, concrete and aggregate block manufacture. However the main uses have been in unbound engineering applications, such as bulk fill in civil engineering projects, highway sub-base and as railway ballast. Figure 3-5 shows the breakdown of the main uses of BA.

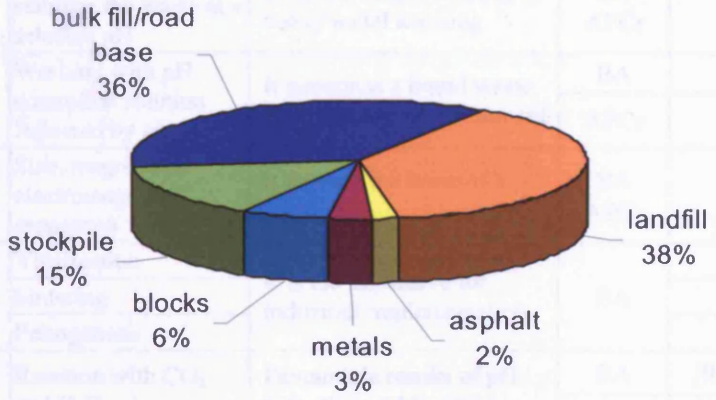

Figure 3-5 Uses of BA in the UK after processing, from 1996 to 2000 [2]

With respect to APCr, due to their hazardous nature they cannot be directly landfilled. In many incineration plants APCr are currently stored in heated bunkers to prevent the hydration of the lime. APCr have high alkalinity, dryness, fine particle size and hence large surface area. These properties make them useful in the treatment of a range of industrial wastes such as non-volatile organic liquids and sludges. The wastes are adsorbed onto or absorbed by the powders, making them a solidified material suitable for conventional landfilling [2].

MSWIr contain oxides, alumina, silica, iron oxide and calcium oxide and other metals. Metals and dioxins are present in MSW and the incineration process produces additional dioxins. The chemical characteristics and the long term behaviour of residues determine their disposal option. There are various treatment options for MSWIr. Table3-8 shows a summary of the current available technologies for MSWIr processing.

Technology	Unit operation	Comment	MSWIr	Ref
Stabilisation/ solidification	Addition of hydraulic binders/pore-filling additives	It is widely accepted but gives problems with leaching and microcracking	BA	[7, 8, 73, 74]
			APCr	[6, 8, 74-79]
Chemical stabilisation	Acid addition to stabilise the waste at a selected pH	It shows variable results of heavy metal leaching	BA APCr	[11, 12]
Washing	Washing with pH controlled solution followed by s/s	It generates a liquid waste that needs further treatment	BA	
			APCr	[80-82]
Physical separation	Size, magnetic or electromagnetic separation	It favours the reuse of a fraction	BA APCr	[74]
Thermal Treatment	Vitrification	It is too expensive for industrial implementation	BA	
	Sintering			[83]
	Petrogenesis			[84]
Carbonation	Reaction with CO_2 and H_2O	Favourable results of pH reduction and leaching	BA	[9, 12, 28, 85]
			APCr	[10, 12, 86-88]
	s/s followed by reaction with CO_2 and H_2O	Improves the leaching behaviour when compared to s/s alone	APCr	[5, 89]
Landfilling	Disposal in selected landfill sites	Limited by current legislation.	BA APCr	

Table 3-8 Summary of methods for treatment of MSWIr

In a study from the UK Environment Agency, accelerated carbonation and acid neutralisation processes were compared as MSWIr management technologies. This study proved carbonation to be the more promising alternative to treat MSWIr. The report concludes that the hazardous properties of incinerator residues can be reduced by carbonation due to consumption of lime and precipitation of calcite. The pH is reduced without significant loss of acid neutralisation capacity, thereby buffering pH and controlling the solubility of major heavy metals [12].

3.3 Conclusion

The factors supporting the use of accelerated carbonation as preferred technology for the treatment of MSWIr can be summarised as follows:

- Favourable chemical characteristics (high concentration of lime and silica)
- Suitable physical properties (particle size and surface area)
- Large and increasing volumes of MSWIr produced in the UK
- More than 50% of MSWIr in the UK is sent to landfill
- Legislation is encouraging the development of sustainable technologies for the treatment of MSWIr
- Accelerated carbonation has been compared to other technologies and has been proven to be more effective in reducing the hazardous nature of MSWIr

CHAPTER 4

4 Background Theory to Model the Kinetics of Carbonation of APCr

4.1 Introduction

The importance of determining a mathematical model to describe the kinetics lies in the practical need to predict the behaviour of the system under untested conditions. The first step to kinetic modelling involves the selection of an appropriate kinetic model subsequent to a primary characterisation of the system. Once this model is known, the following step is the determination of the mechanism controlling the rate of reaction. Then, the mathematical expression describing the experimental data is derived, in terms of a kinetic triplet (i.e. the two Arrhenius parameters and the conversion function). The final stage is to relate the results to the actual sequence of physico-chemical processes occurring, namely the reaction mechanism.

Mathematical models describing the carbonation process have been developed in the past for hydrated cementitious systems [90, 91]. There are numerous studies on the mechanisms of carbonation of concrete and concrete components, as this phenomenon is one of the many important factors determining the service life of a concrete structure [49, 91-96]. There are also kinetic studies on the carbonation of complex systems in solution, such as magnesia (MgO) slurries [97].

The kinetics of the reaction of lime and calcium hydroxide with CO_2 at low temperatures have been studied in relation to the application of lime to CO_2 separation from flue gas [98, 99]. However, the kinetics of carbonation of non-hydrated complex systems such as APCr have never been studied. Only the relative importance of carbonation factors on metal mobility of APCr has been previously reported [10, 87].

4.2 Classification of Chemical Reactions of Solids

As a generalised scheme, Table 4-1 summarises the most frequently observed kinetic characteristics for the reactions of a solid alone, or with a gas, a liquid, or another solid.

Reaction	Mechanism	Kinetic characteristics
Decomposition of a single solid	Nucleation →Growth	Interface phenomena Geometric control
Reaction of a solid with a gas	Reaction at immobile surface	Interface control Diffusion control
	Nucleation →Growth	No barrier layer Interface phenomena Geometric control
	Barrier layer formation	Diffusion across barrier control
Reaction of a solid with a liquid	As with solid and gas	Diffusion in the liquid may be important, particularly where no barrier layer is formed
Reaction of a solid with a solid.	As with solid and gas	Normally the immobility of reactants inhibits reaction and barrier layer formation

Table 4-1 Reaction pathways and their relation to kinetic characteristics [100]

The processes controlling the rate of product formation are known to be [100]:

- A chemical reaction at an advancing interface (following a nucleation step)
- A chemical reaction at a static interface (following diffusion of species to that interface)
- Diffusion of reactants in an homogeneous phase or across a layer of product to the reaction interface in which the chemical step is fast. The influence of diffusion generally increases with the reaction rate (gas > liquid > solid), the extent of reaction, the particle size, etc.

Based on the phase combination of the reactant and the product, the carbonation of MSWIr is an heterogeneous reaction of the following kind:

$$A_{(g)} + S_{(s)} \longrightarrow \text{fluid and solid products} \qquad (4.1)$$

The newly formed solid products replace the original particles as the reaction proceeds. Since the amount of reactant surface and its availability change with the extent of reaction, the overall reaction rate changes with time.

When a component of a gas reacts with a solid, the reaction occurs at an active site of the solid. First the gas molecule is transported to the surface of the solid. Then, it diffuses into the particle to an active site and adsorbs at the site where the surface reaction takes place. As a result the solid particle remains unchanged in size during the reaction, as shown in Figure 4-1,

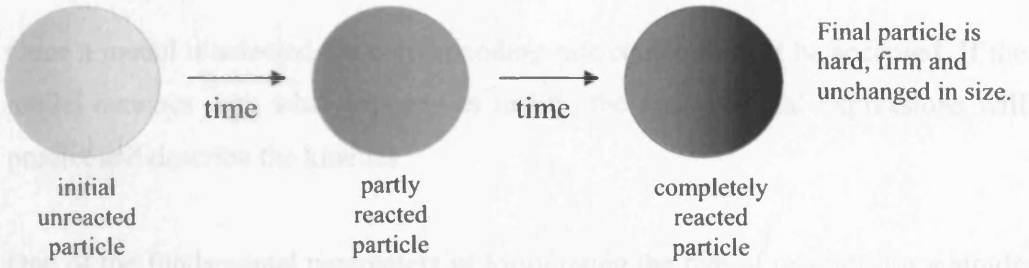

Figure 4-1 Behaviour of reacting solid particles [101].

As a basis for the interpretation of kinetic behaviour of these systems, the following five general kinetic principles have been accepted [100]:

i. The rate of reaction of a solid is proportional to the aggregate effective area of the reactant-product interface.
ii. The rate of advance of the interface through an isotropic reactant under isothermal conditions is constant. This and the previous principle are valid whenever the solid product does not represent a significant barrier and there is no systematic change in the composition.
iii. The dependence of the rate constant on the temperature obeys the Arrhenius equation.
iv. When one or more product phases are a barrier layer to the contact between reactants, the overall rate may be controlled by the diffusion of species through the barrier and influenced by geometrical factors.
v. The rate of reaction of a solid with a gas may also be a function of the concentration of the gas. For experimental studies then, it is necessary to ensure that there is uniform availability of the gas to obtain significant kinetic measurements of the chemical step. Otherwise, diffusion rates will control the overall rate of reaction. This effect is magnified in systems with finely divided solids.

4.3 Selection of a Kinetic Model

"The requirement for a good engineering model is that it be the closest representation to reality which can be treated without too many mathematical complexities" (Levenspiel) [101].

Once a model is selected the corresponding rate equation must be accepted. If the model matches with what happens in reality, the mathematical expressions will predict and describe the kinetics.

One of the fundamental parameters in formulating the rate of reaction for a single particle is how the active sites and surface areas for adsorption of the gas molecules are distributed. Porosity has a key effect on this parameter. Accordingly there are three models to consider [102]:

The shrinking core model (see Figure 4-2): If the reactant is non-porous, the reaction occurs at first in the outside layer of the particle and the reacted front advances into the solid. Then, at any time there is an unreacted core of material which shrinks in size during the reaction. A porous particle might also behave this way if the resistance to reaction is much less than the resistance to diffusion of fluid reactant in the pores of the particle. The key factor in this model is that the reaction always occurs at the interface between unreacted core and solid product.

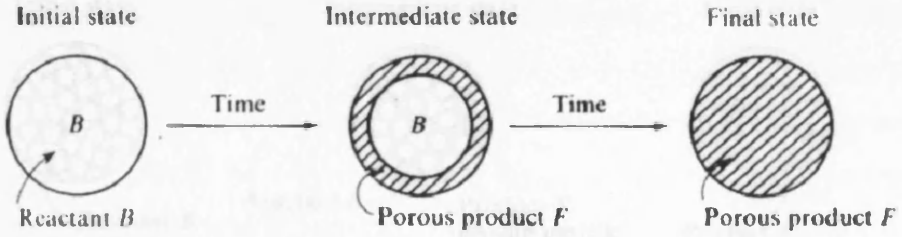

Figure 4-2 Shrinking core model [102]

The progressive-conversion model (see Figure 4-3): The gas enters and reacts throughout the particle at all times, most likely at different rates at different locations within the particle. Thus, the solid reactant is converted continuously and progressively throughout the particle. This would be the case of a highly porous reactant, in which the gas can reach all parts of the solid without diffusion resistance.

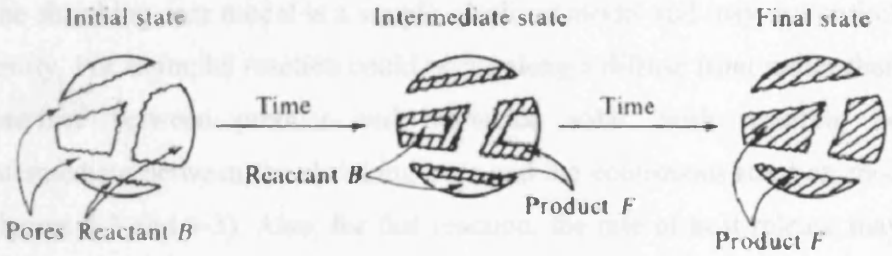

Figure 4-3 Progressive conversion model [102]

The grain model or particle-pellet model (see Figure 4-4): This would be the case of solid formed by compression of non porous particles into a porous pellet. The pores around the particle are small enough to generate a decreasing profile of gas concentration towards the centre of the particle. This is the intermediate case between the two explained above. Here, the overall reaction rate depends on the distribution of the non-porous particles in the pellet, the structure of said pellet, the intrinsic reaction velocities and the transport properties of fluid reactants in the solid [103].

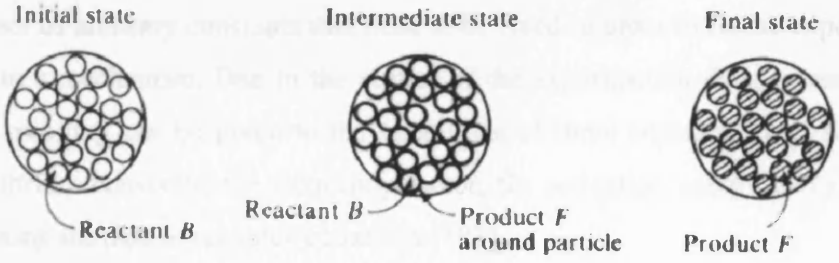

Figure 4-4 Porous pellet composed of non-porous particles. Pellet model [102]

The three models have been used to represent the effect of mass transport on the global rate of reaction. The grain model case is perhaps the most realistic, involving conservation equations for both the particles and the pellets. However, the shrinking core model is quite representative of what happens in reality with many solid-gas reactions.

The shrinking core model is a simple idealised model and may not entirely match reality. For example, reaction could occur along a diffuse front rather than a sharp interface between product and unreacted solid, with resulting behaviour intermediate between the shrinking core and the continuous reaction models (see Figures 4-2 and 4-3). Also, for fast reaction, the rate of heat release maybe high enough to cause temperature gradients within the particles or between particle and the gas [101]. However, despite these problems, it is concluded on the basis of numerous studies [103-105] that the shrinking core model is the best simple representation for most reacting gas-solid systems.

4.4 Unreacted-core-shrinking Model for Spherical Particles

4.4.1 Order of Reaction

When the process is controlled by the chemical reactivity of the solid reactant, it is possible to qualitatively describe the mechanism of reaction based on the Langmuir adsorption isotherm. However, in many cases there may be a significant number of arbitrary constants that need to be fixed in order to fit the experimental data to a mechanism. Due to the scatter of the experimental data, in many cases little meaning can be given to the magnitude of these constants (e.g. adsorption equilibrium constants, the frequency factor, the activation energy, etc.) obtained by fitting the data to complex equations [103].

The nth-order rate equation can fit the data when the chemical reaction step controls the process. Based on adsorption isotherms, the order of reaction can be shown to vary from zero to two, depending on whether the gas is strongly adsorbed or weakly adsorbed [101].

The rate of reaction for fluid component A, r_A, and for solid reactant S, r_S, can then be written as:

$$r_A = a\, r_S = -a\, k_s C_s^m C_A^n \text{ or } -a\, k_v C_S^m C_A^n \tag{4.2}$$

where

a is the stoichometric coefficient of the gas reactant

m is the order of reaction with respect to solid reactant S

n is the order of reaction with respect to gas reactant A

k_s k_v is the reaction rate based on the reacting surface area and reacting solid volume

r_A is the rate of reaction expressed in mol/s m^2

Most reactions at a solid surface cannot be reversible, so they are not considered. The reason for this is that the phenomenon of solid deposition in the reverse reaction does not provide the solid product with a structure identical to the initial solid reactant in the forward reaction [103].

4.4.2 Formulation of the Model for Particles with Constant Radius

The gas reacts generating a porous product layer around the unreacted densely packed solid. In a spherical particle, the external radius r_p remains the same, assuming no deformation of the product layer that has been formed. Figure 4-5 shows the resistances in series that the gas has to move through to reach the surface of the unreacted core (i.e. fluid film, porous product layer and reaction surface) and the concentration profiles within the particle.

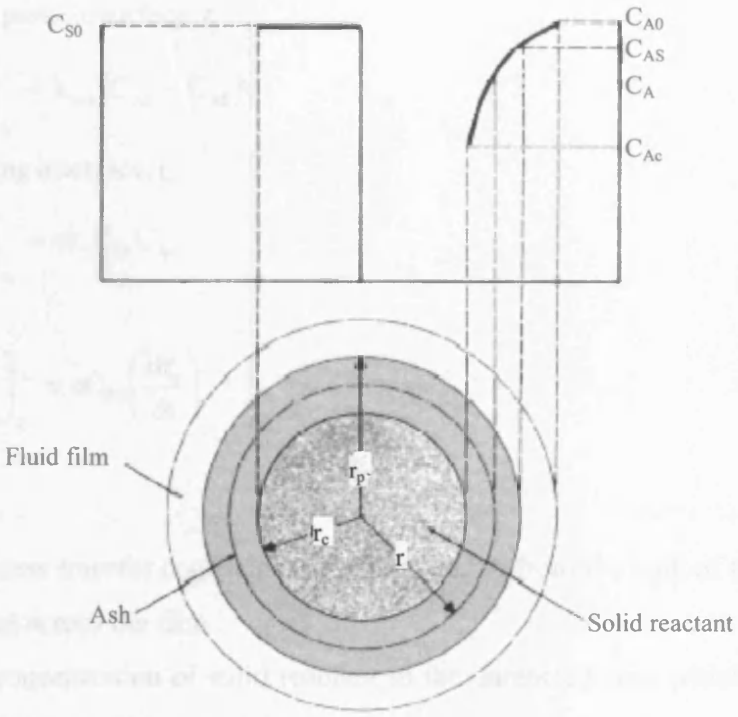

Figure 4-5 Schematic diagram of concentration profile for the unreacted-core shrinking model [103]

where

C_{A0} concentration of gas reactant A in the bulk of the fluid stream

C_{AS} concentration of gas reactant A at the surface of the particle

C_{AC} concentration of gas reactant A at the surface of the core

r_p radius of the particle

r_C radius of the unreacted core

r radius at any point from the centre of the particle

The fundamental equation for the material balance of A is the following [101-103, 106]:

$$\varepsilon \frac{\partial C_A}{\partial t} = D_{eA}\left(\frac{\partial^2 C_A}{\partial r^2} + \frac{2}{r}\frac{\partial C_A}{\partial r}\right), \qquad r_p > r > r_C \tag{4.3}$$

The initial condition is $r_C = r_p$ at $t = 0$

The boundary conditions for a spherical particle are:

at the solid particle surface, r_p

$$D_{eA}\left(\frac{\partial C_A}{\partial r}\right)_{r_p} = k_{mA}(C_{A0} - C_{AS})$$

at the moving interface, r_c

$$D_{eA}\left(\frac{\partial C_A}{\partial r}\right)_{r_C} = ak_s C_{S0} C_{Ac}$$

and

$$-D_{eA}\left(\frac{\partial C_A}{\partial r}\right)_{r_C} = aC_{S0}\left(\frac{dr_c}{dt}\right)$$

(4.4)

where

k_{mA} is the mass transfer coefficient of component A from the bulk of the gas to the solid surface across the film

C_{S0} is the concentration of solid reactant in the unreacted core which is assumed to be constant for uniform particles

ε is the voidage of the porous layer of product of the particle

The reaction considered is equivalent to a first order reaction with respect to gas A and zero order reaction with respect to solid reactant S. The solution of equation (4.3) with the boundary conditions given by equations (4.4) gives the concentration profile of A as a function of particle radius, r, and time, t. However, an analytical solution of these equations cannot be obtained except in a few special cases. It is therefore usual to let:

$$\varepsilon \frac{\partial C_A}{\partial t} = 0 \tag{4.5}$$

to obtain an approximate solution. This technique is known as the pseudo-steady-state and is valid for most of the solid-gas reaction systems except for those with extremely high pressure and very low solid reactant concentration.

The concentration profile and the time required for the particle to reduce the unreacted core from r_p to r_C are given by:

$$\frac{C_A}{C_{A0}} = \frac{\left(1+\frac{D_{eA}}{ak_sC_{S0}r_c}\right)\frac{1}{r_c}-\frac{1}{r}}{\left(1+\frac{D_{eA}}{ak_sC_{S0}r_c}\right)\frac{1}{r_c}-\left(1-\frac{D_{eA}}{k_{mA}r_p}\right)\frac{1}{r_p}} \tag{4.6}$$

$$t = \frac{ar_pC_{S0}}{C_{A0}}\left[\frac{1}{3}\left(\frac{1}{k_{mA}}-\frac{r_p}{D_{eA}}\right)\left(1-\frac{r_c^3}{r_p^3}\right)+\frac{1}{ak_sC_{S0}}\left(1-\frac{r_c}{r_p}\right)+\frac{r_p}{2D_{eA}}\left(1-\frac{r_c^2}{r_p^2}\right)\right] \tag{4.7}$$

At complete conversion when $t = \tau$ and $r_c = 0$, equation (4.7) becomes:

$$\tau = \frac{ar_pC_{S0}}{C_{A0}}\left(\frac{1}{3}\frac{1}{k_{mA}}+\frac{1}{ak_sC_{S0}}+\frac{r_p}{6D_{eA}}\right) \tag{4.8}$$

The resistances in the denominator represent the three resistances in series. For the gas to react it must diffuse through the gas film and the product layer to the surface. The conversion x is given by:

$$x = 1-\frac{\left(\frac{4}{3}\right)\pi r_c^3}{\left(\frac{4}{3}\right)\pi r_p^3} \tag{4.9}$$

Expressing the reaction time in terms of conversion, the solutions to the three different cases are as follows:

When the gas film controls the rate of reaction, $k_{mA} << D_{eA}, k_s$, then:

$$t = \frac{ar_pC_{S0}}{3k_{mA}C_{A0}}x \tag{4.10}$$

For the case of reaction rate controlled by the diffusion through the product, $D_{eA} << k_s, k_{mA}$, then:

$$t = \frac{ar_p^2C_{S0}}{6D_{eA}C_{A0}}\left[1-3\left(1-x\right)^{2/3}+2\left(1-x\right)\right] \tag{4.11}$$

When the chemical reaction controls the rate, $k_s << D_{eA}, k_{mA}$, then:

$$t = \frac{r_p}{k_s C_{A0}}\left[1 - (1-x)^{1/3}\right] \qquad (4.12)$$

4.5 Determination of the Rate-controlling Step

A primary objective of most fundamental kinetic investigations is to identify the rate-limiting process. The kinetics and rate-controlling steps of a solid-fluid reaction are deduced by noting how the progressive conversion of the solid is influenced by the main parameters defining the systems (i.e. temperature, particle size, concentration).

A surface reaction in solid-fluid systems comprises the following steps [101, 102]:

1st. Diffusion of gaseous reactant through to the surface of the solid.

2nd. Penetration and interparticle diffusion of the gas through the product to the reaction surface.

3rd. Adsorption at an active site of the solid reactant.

4th. Reaction of the gas with the solid at the reaction surface.

5th. Diffusion of the gaseous products (if any) to the exterior surface of the solid.

6th. Diffusion of the gaseous products through the gas film back into the main body of fluid.

In the case of irreversible reactions (e.g. carbonation), where gaseous products are not formed, the 5th and 6th steps do not take place. Thus, the first four steps will usually determine the global rate of reaction. The one presenting the highest resistance will be the rate-controlling step. Therefore, there are three possible controlling steps:

- Diffusion through gas film controls
- Diffusion through product layer controls
- Chemical reaction controls

As seen in 4.4.2, a mathematical expression can be derived for each case and for particles of different size. The majority of solid-fluid reactions are influenced simultaneously by more than one step. The relative importance of the gas film, product layer and chemical reaction varies depending on the conversion. For a

particle of constant size, the resistance to reaction gets higher as the surface of the unreacted core decreases, whilst resistance to diffusion through the product increases as reaction progresses. In these situations, the different resistances will have to be combined.

Figure 4-6 shows the progressive conversion of spherical solids with chemical reaction, film diffusion, and diffusion through the layer of product in turn controlling the reaction rate. The comparison of kinetic experiments with the predicted curves will indicate the actual rate-controlling step.

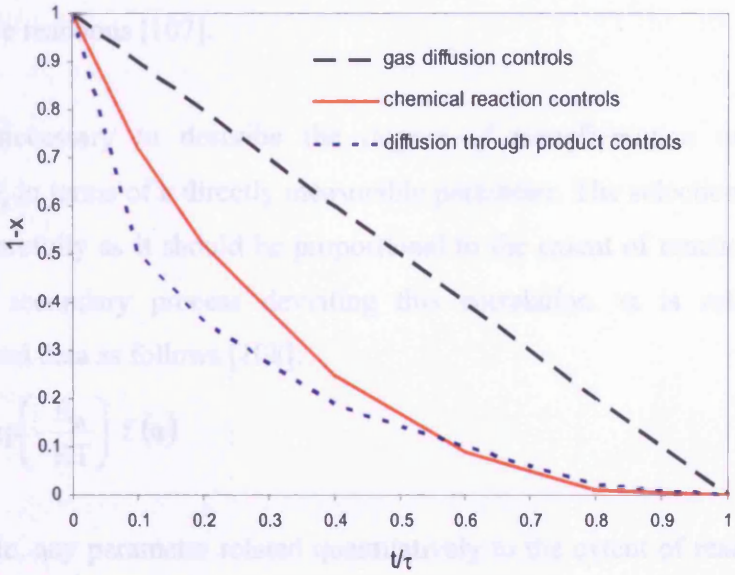

Figure 4-6 Progress of reaction of a single spherical particle with a gas measured in terms of time for complete conversion for particles of constant size [101], where x is the reaction conversion and τ is the time at complete conversion

In practical systems it is difficult to make a rigorous analysis. There are problems of changing size and shape of the solid during the reaction and formation of a product around the reactant that could cause cracking. In addition, the complex velocity profile of the surrounding fluid makes the problems of mass and energy transfers to the solid reactant more difficult to treat [103].

4.6 Kinetic Expressions for Diffusion-limited Reactions

Carbonation is known to be a diffusion controlled reaction [17, 42]. In a diffusion limited reaction, the overall rate is determined by the movement of one or more reactant species to, or a product from, a reaction interface [100].

The search for a mathematical description of the data is usually sought in terms of a "kinetic triplet", that is the Arrhenius parameters, frequency factor (A) and activation energy (E_A), and the reaction model. It is also important to identify the kinetic scheme that differentiates between one-step, multi-step, parallel and consecutive reactions [107].

First, is necessary to describe the *degree of transformation* or *fractional reaction,*α, in terms of a directly measurable parameter. The selection of α has to be done carefully as it should be proportional to the extent of reaction and there could be secondary process deviating this correlation. α is related to the experimental data as follows [108]:

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E_A}{RT}\right) f(\alpha) \tag{4.13}$$

In principle, any parameter related quantitatively to the extent of reaction can be used for rate studies, though, in practice, gas pressure evolution, mass change and enthalpy changes have been most widely used.

When the reaction is carried out at constant temperature, integration of (4.13) gives:

$$g(\alpha) = \int_0^{\alpha} \frac{d\alpha}{d\, f(\alpha)} = \int_0^{t} k(T)\, dt \tag{4.14}$$

The expressions of $g(\alpha)$ corresponding to the most widespread diffusion controlled mechanisms for the kind of system under study are given below. The following rate equations have been developed from studies of gas-solid reactions by assuming that particles of solid reactant are completely covered by a layer of product.

The simplest kinetic law, when the surface area is constant and the decrease of reaction rate is due to the thickness of the barrier layer, is the *parabolic law*:

$$\alpha = (k_A\, t)^{1/2} \tag{4.15}$$

This expression governs one dimensional diffusion processes with constant diffusion coefficient [109]. It is known to be valid in many cases for the oxidation of metals sheets [100].

Variations in behaviour are apparent when diffusion in the barrier layer is inhomogeneous due to cracking that may be produced by the development of more than one product layer. Alternative rate relations can be used, such as the *logarithmic law*:

$$\alpha = k_1 \log(k_2\, t + k_3) \tag{4.16}$$

and the *linear law*:

$$\alpha = k_1\, t + k_2 \tag{4.17}$$

The rate expression for a two-dimensional diffusion controlled reaction in a cylinder of radius r is the *Holt-Cutler-Wadsworth equation*:

$$(1-\alpha)\ln(1-\alpha) + \alpha = \frac{k_1}{r^2}\, t \tag{4.18}$$

There are modifications of this expression that include consideration of reactions in which the volume of product is different from that of the reactant from which it was derived. When the reaction is starting on the exterior of a spherical particle of radius r, the derived expression is the *Jander equation*:

$$\left[1-(1-\alpha)^{1/3}\right]^2 = \frac{k}{r^2}\, t \tag{4.19}$$

A modification of the previous expression results in the *Ginstling-Brounshtein equation*:

$$\left(1-\frac{2\alpha}{3}\right) - (1-\alpha)^{2/3} = \frac{k}{r^2}\, t \tag{4.20}$$

If there is a change in molar volume between the reactant and the product, (ratio, z^{-1}) the *Carter equation* is derived:

$$\left[1+(z-1)\alpha\right]^{2/3}-(z-1)(1-\alpha)^{2/3}=z+2(z-1)\frac{k}{r^2}t \qquad (4.21)$$

Equation (4.21) is obeyed in the oxidation of spherical particles of nickel with homogeneous diameters. When volume ratio is unity, equation (4.21) reduces to (4.20).

When the rate of interface advance under diffusion control is also proportional to the amount of unreacted substance present, the *Zhuralev-Lesokhin-Tempelman equation* is obtained:

$$\left[(1-\alpha)^{-1/3}-1\right]^2=\frac{k}{r^2}t \qquad (4.22)$$

The *Dunwal-Wagner equation* is based on the application of Fick's second law of diffusion into or out of a sphere (radius r):

$$\ln\left\{\frac{6}{\pi^2(1-\alpha)}\right\}=\frac{\pi^2 D}{r^2}t \qquad (4.23)$$

where

D is the diffusion coefficient of the migrating species.

The hypothesis that reaction in many powder mixtures is initiated at interparticle contact and that product formation occurs by diffusion through these contact zones can be expressed by the *Komatsu-Uemura equation*. In this model the reactant is not covered with a layer of product [110]:

$$\left[(1+\alpha)^{1/3}-1\right]^2=\frac{k}{r^2}t \qquad (4.24)$$

The reactions can also proceed by a nucleation and diffusion controlled growth process. A solid solution is generated at first and then the product precipitate deposits at the interface between the reactants, after an initial induction period. The nuclei of products are produced at the surfaces of the initial solid particles

and growth may occur with or without maintained nucleation. For these reaction models the interface advance follows the parabolic law (i.e. is proportional to $(Dt)^{1/2}$) [100].

There are several possibilities:

- Nucleation is instantaneous ($\beta = 0$)
- Nucleation is constant ($\beta = 1$)
- Nucleation is deceleratory ($0 < \beta < 1$)

For nuclei growing in one, two or three dimensions ($\lambda = 1$, $\lambda = 2$, $\lambda = 3$ respectively). The expressions have the following general form:

$$-\log(1-\alpha) = (k\,t)^m \qquad (4.25)$$

where

$m = \beta + \lambda / 2$ for diffusion controlled reactions, Table 4-2 shows the values of m depending on the growth model. β and λ are factors describing the rate of nucleation and the dimensions in which nuclei grow.

Model	Nucleation rate	m
One-dimensional growth	Constant	1.5
	Zero (instantaneous)	0.5
	Deceleratory	0.5-1.5
Two-dimensional growth	Constant	2.0
	Zero (instantaneous)	1.0
	Deceleratory	1.0-2.0
Three-dimensional growth	Constant	2.5
	Zero (instantaneous)	1.5
	Deceleratory	1.5-2.5

Table 4-2 Values of exponent m for equation (4.25) [100]

Measurement of m does not guarantee the identification of the reaction mechanism. In addition, it cannot essentially differentiate between diffusion or interface limited reaction models. All the accumulated evidence and uncertainties have to be assessed, therefore additional independent evidence is needed to support the mechanism proposed.

To compare experimental data with the equations above, it is convenient to use a reduced time scale such as $t/t_{0.5}$, where $t_{0.5}$ corresponds to $\alpha = 0.5$. Then for each model, single curves of α versus $t/t_{0.5}$, can be calculated and are directly

comparable to experimental data for all values of temperature, pressure and other variables for which the specific $g(\alpha)$ remains valid. The dependence of α on these variables is contained in the parameter $t_{0.5}$ [109, 111].

To distinguish between the different models requires considerable accuracy, and for powder systems particles of uniform shape and size should be used. This condition can rarely be satisfied. Thus, for every model, parallel microscopic observations help to establish the interface geometry and spectroscopic and X-Ray Diffraction measurements give more detailed characterisation of the phases present [108].

Reactions in the solid state, such as carbonation, usually have a multistep nature, which would imply the combination of two or more kinetic models. Therefore, depending on the considered reaction performed at different temperatures, the choice of the kinetic models influences the selection of the reaction mechanism [107].

Systems of nature similar to that of carbonation of MSWI APCr have been found to carbonate following the above kinetic models [112]. For example Nishikawa et al. [92] found that the carbonation of synthesised ettringite ($3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}32H_2O$) could be modelled by the Jander equation, whilst Goñi et al. [49] describe the accelerated carbonation of Friedel's salt ($Ca_4Al_2O_6Cl_2{\cdot}10H_2O$) in calcium aluminate cement paste, as governed by the parabolic law.

4.6.1 Influence of Particle Size Distribution on Kinetics

The formulation of kinetic expressions is usually done on the basis of a specified geometry and mechanisms of reaction often assume particles to be of a regular, defined shape and of uniform size. Equations developed like this have given a suitable representation of observed isothermal kinetics of a variety of reactions. Some authors have questioned the suitability of the α-t curve to describe the reaction model, due to limitations induced by the particle size distribution [113]. Other authors have introduced in the model allowance for particle size distribution [101, 114].

Variations in the particle size can cause appreciable effects in the kinetic characteristics of a solid reaction, especially for diffusion-controlled reactions. At short times, the value of α is increased relative to that based on uniform particle size, due to the faster reaction of the smaller particles. On the other hand, at later stages, α is lower than for a uniform system, due to the slowest reaction of larger particles [100].

4.7 Variation of Reaction Rate with Temperature

As shown in equation (4.26), reaction rates are related to α and to temperature, T, by different and independent functions and a complete kinetic description of behaviour requires characterization of both expressions:

$$\frac{d\alpha}{dt} \propto f(\alpha)k(T) \tag{4.26}$$

Reaction rates are known to increase with temperature. The best way of measuring the influence of T is to separate variables by first determining isothermal curves at different T and expressing each set of observations in the form [100]:

$$g(\alpha) = k\,t \tag{4.27}$$

The relationship between k and T has been usually assumed to obey the Arrhenius equation:

$$k = A \exp\left(-\frac{E_A}{RT}\right) \tag{4.28}$$

where

A is the frequency factor

E_A is the activation energy

R is the gas constant (R = 8.3145 J/mol K).

This approach is widely accepted and independent of the physical meaning of A and E_A, is a well-established method of comparing kinetic data. However, in the field of solid reactions, the Arrhenius equation is generally not considered

particularly reliable and the results produced under this approach have been the subject of numerous criticisms.

Plots of log k versus T^{-1} are quite insensitive. Besides, the influence of systematic errors in the fit of the data to the equation and the magnitudes of measured values of A and E_A, are not easily apparent. In solid reactions there is little known about alternative relationships to Arrhenius but some studies have shown that this model is not necessarily the only or the best relation for all reactions [100].

4.7.1 Significance of Arrhenius Parameters

The Arrhenius parameters determined for reactions of solids are frequently described using analogy with gas processes by the collision theory [101]:

- The activation energy E_A is identified as the energy barrier that has to be overcome during the transformation of reactants into products during the rate limiting step.
- The frequency factor A is determined with the theory of occurrence of molecular collision leading to reaction of the reaction configuration which is first identified as a molecular encounter.

When dealing with reactions in the solid state, the collision theory is unsustainable between species that are immobilised in the lattice of a solid. Therefore, when the Arrhenius expression is used in heterogeneous processes, an alternative theoretical basis must be provided. One possibility is to use the absolute reaction rate theory, in which the activated complex is considered as a high energy atomic configuration [100].

Considering that k has contributions from nucleation and growth processes, the determination of the Arrhenius parameters is influenced by the empirical selection of the kinetic model used to find k. This is one of the main disadvantages of using this method to determine the rate constant. Some authors maintain that the empirical E_A obtained in this way, may depend on the choice of the rate equation [112], while others affirm that the measured value of E_A is usually insensitive to the particular rate expression selected [100].

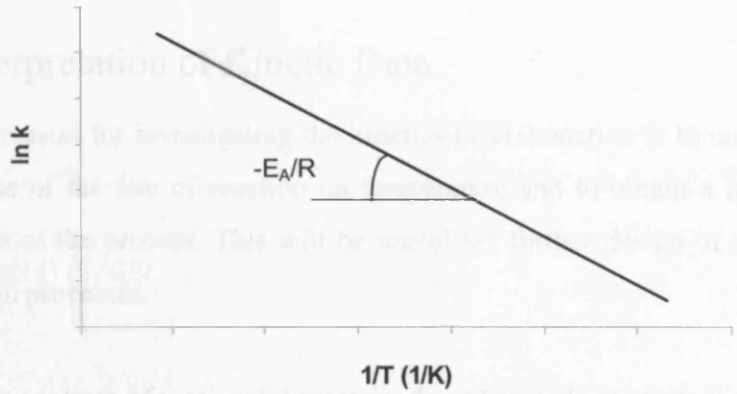

Figure 4-7 Arrhenius plot

Figure 4-7 shows the Arrhenius plot. The slope of the Arrhenius plot has units of $[T^{-1}]$ and the E_A is expressed as kJ/mol. Some authors propose that E_A is the average excess energy that a reactant molecule must posses to react. Others see A and E_A as having empirical rather than theoretical significance, and both must be reported to define the reaction rate. Other authors consider E_A as a complex function of multiple parameters, including deviations from equilibrium and thermal gradients [100].

In general, the fundamental significance of E_A to a transformation has to be given with caution. It is a measure of the temperature dependence of the rate of reaction carried out under a certain set of experimental conditions. Before extrapolating this value to a different set of conditions, it is necessary to demonstrate that the mechanism is still the same as that operating during the experiment [112, 115].

4.8 Interpretation of Kinetic Data

The main reason for investigating the kinetics of carbonation is to understand the dependence of the rate of reaction on temperature and to obtain a mathematical description of the process. This will be useful for further design of a continuous carbonation processes.

The kinetic analysis of a gas-solid reaction should provide the following:

- The best (a) kinetic models (type of model and reaction order), (b) Arrhenius parameters (pre-exponential factor -A- and activation energy – E_A-), (c) kinetic scheme.
- The goodness of fit.
- The possibility of retrieving the kinetics of a simulated reaction for which the kinetic model and Arrhenius parameters are unknown.

However, the demonstration that a set of (α_i, t_i) values obeys a particular kinetic expression is not an absolute proof of the reaction mechanism for which the rate equation $f(\alpha)$-t is derived. Therefore every interpretation should always be supported by independent analytical evidence, such as microscopic observation [100].

The kinetic model of APCr accelerated carbonation will be developed in Chapter 6 and evidence supporting the model will be shown.

CHAPTER 5

5 Materials Characterisation, Experimental Equipment and Methods

5.1 Characterisation Techniques

Prior to carbonation the MSWIr were analysed to determine the major physical and chemical properties. In addition, a series of analytical techniques were applied to evaluate the property changes induced by carbonation.

Particle size distribution

The particle size distributions of BA and APCr were obtained by weight percentage passing sieves. For the BA, the particles were first ground to pass the 2mm sieve and any major pieces of glass and metal were removed prior to the sieving.

Moisture content

The amount of water present in the BA and APCr as received was measured by weight difference of the ash before and after drying. The ashes were dried using an oven at 105 °C (BS 1377-2 1990).

Composition

The composition of the ash was determined using X-Ray Fluorescence (XRF) analysis. The analysis of the first set of BA and APCr was carried out at Churchill Laboratories in Newcastle-under-Lyme and Crawcrook Laboratory in Crawcrook and was provided by Ballast Phoenix. The analysis of the APCr from SELCHP was conducted on a Minipall II energy dispersive XRF with 30KeV Rh tube at the University of Brighton.

Mineralogy

The analysis of the mineral phases on BA and APCr was carried out through X-Ray Diffraction (XRD) using a diffractometer Siemens Kristalloflex 810 with a

Cu anode generator in the range from 0 to 75 degrees 2θ. The settings fixed for the generator were 40kV and 40mA. For powders, XRD is the most suitable method for identification of polycrystalline phases and it can also give information on the degree of crystallization of the solid. The ashes were ground to ensure homogeneity of the samples which were then pressed into a sample holder so that there was a smooth flat surface on which to conduct the analysis.

Morphology

The examination of the morphology of the ash was carried out using a JEOL JSM-5310 Scanning Electronic Microscope (SEM) with both secondary electron and back-scattered imaging. Backscatter images have contrast depending on the average atomic number of the elements in the material. To make the samples electrically conducting, a thin layer of gold vapour was deposited onto the samples.

Carbonate content

The carbonate decomposition behaviour was observed through the thermogravimetric and differential thermal analysis (TG/DTA) of carbonated APCr. The equipment used was a Stanton Redcroft STA-780 thermo-analyser. The experiments were carried out on a temperature range of 20-1100°C at a heating rate of 10°C/min. The carbonate content of the ashes was calculated from the weight loss on ignition between 450°C and 900°C.

Density

The density of the APCr and the BA for the first set of experiments was measured by means of a water pycnometer. In this test the solid was submerged in a known volume of water. The bulk density is calculated based on the volume of water displaced.

Pore structure

The change in porosity, tortuosity and total pore area was measured by means of a mercury porosimeter Micrometrics AutoPore IV 9500 V1.03. The experiments were carried out at an advancing and receding contact angle of 130° and a

mercury filling pressure of 1.32 psi. Mercury porosimetry is a relatively rapid method. It characterizes the pore structure by calculating the pore area and volume distributions according to size, total pore volume, total pore surface area, median pore diameter and sample bulk and apparent densities. These material properties allow other characteristics to be ascertained and reported e.g. permeability and tortuosity. With the method, only pores that reach the surface of the sample can be determined. Samples of a fine pore structure are difficult to degas and adsorbed layers reduce effective pore diameter and pore radius values. During measurement, high pressures to force mercury into small pores, may compress the sample and this can be observed as a too large volume of small or medium sized pores. The volume of the smallest pores is overestimated due to interconnected pores. Mercury porosimetry is therefore a limited technique, however is widely used for powders characterisation.

5.2 Carbonation Chambers

The optimum conditions for carbonation were ascertained by carbonating the ash in stainless steel chambers ((1) in Figure 5-1). Their maximum working pressure is 10 bars. The CO_2 is continuously fed from a gas cylinder (2) at 3 bars. The inlet valves of the chambers (3) are left open so that the pressure is maintained constant at the selected pressure throughout the reaction. Each chamber is equipped with an analogue pressure gauge that monitors the pressure inside (4).

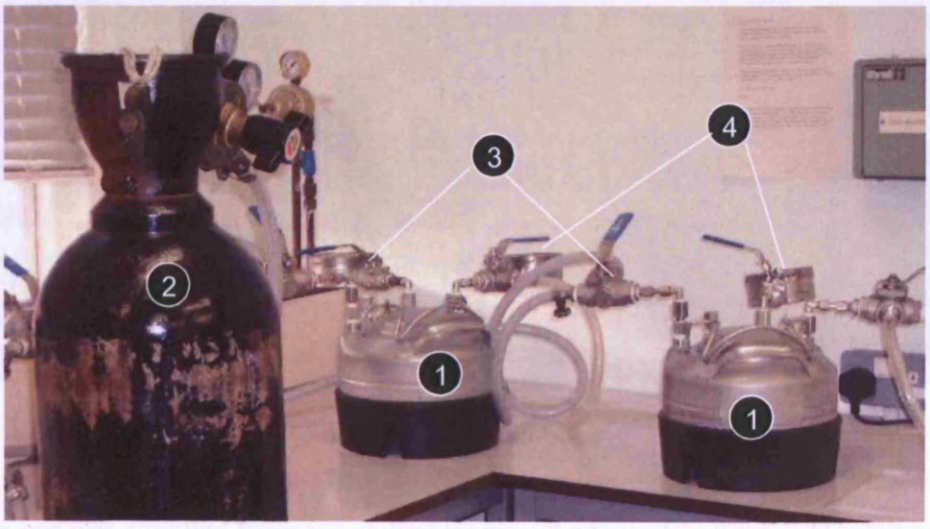

Figure 5-1 Carbonation chambers

Inside the chambers there is a metallic net on which the samples are left to react, see Figure 5-2. The samples are placed in cylindrical plastic holders of 9ml capacity (1). Below the net (2), there is a 150ml crystallising basin (3) with a solution of NaCl in equilibrium that maintains the relative humidity constant in the chamber at 65%. When empty, the chambers are left under pressure of CO_2 to ensure the NaCl solution remains saturated in CO_2.

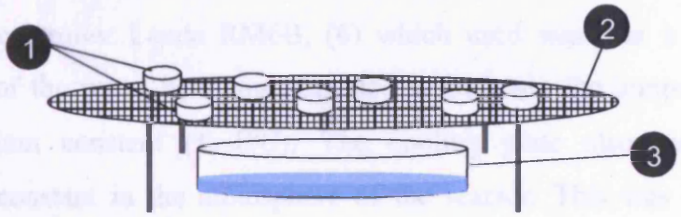

Figure 5-2 System inside the carbonation chambers

5.3 Carbonation Rig

A 5 litre reaction chamber, incorporating a cooling plate, was used to ascertain the kinetic parameters of the carbonation reaction. Figure 5-3 shows the experimental rig, designed and built at University College London.

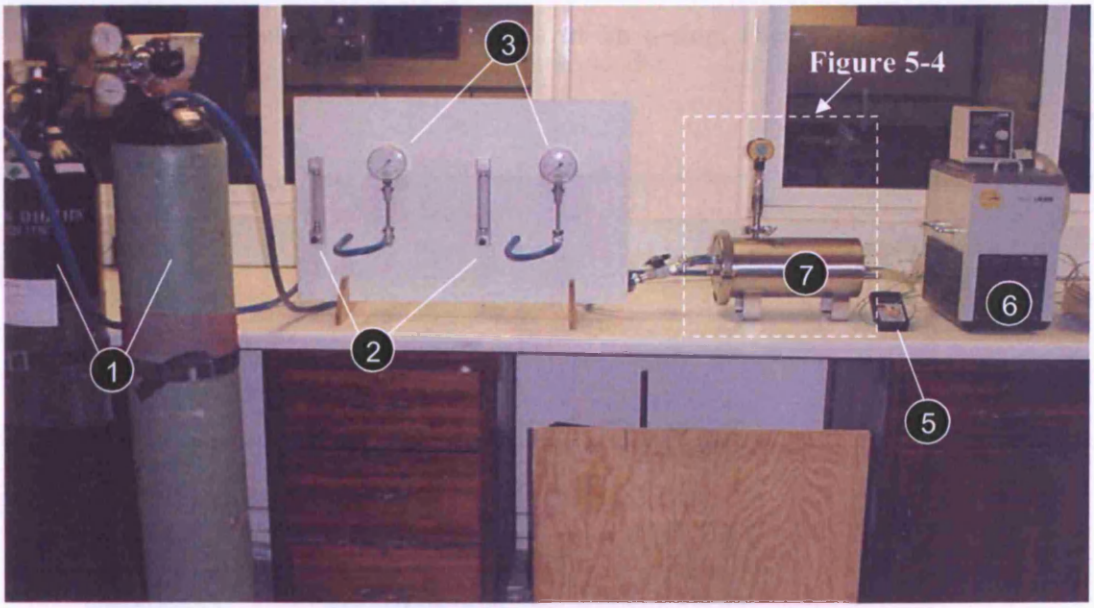

Figure 5-3 Carbonation rig

The gas was supplied from two cylinders placed adjacent to the rig, (1). Nitrogen and CO_2 were mixed before entering the reactor, in order to vary the desired

concentration of the reactant gas. The chosen ratio of gases could be adjusted by means of two flowmeters (2) placed after each cylinder or by feeding them consecutively up to the selected pressure (3 bars).

The stainless steel vessel (7) had a cooling plate inside to control the temperature of the solid throughout the reaction. The cooling plate was connected to a temperature controller Laude RM6B, (6) which used water as a coolant. The temperature of the water bath, was adjusted to maintain the temperature of the reaction system constant (± 1°C). The cooling plate also maintained the temperature constant in the atmosphere of the reactor. This was important, as enthalpy changes during the reaction can cause temporary deviations from the isothermal conditions. The reactor had ports for a digital pressure gauge and a temperature probe, (4) and (5), respectively. Saturated solutions of NaCl and $Na_2Cr_2O_7 \cdot 2H_2O$ were used to maintain the relative humidity at levels of 65% and 45%, respectively.

The reactor has ports for the digital pressure gauge, (1) in Figure 5-4, the temperature probe (2) and the inlet and outlet of the gas (3). The lid is secured with a clamp (4) and is sealed by means of an o-ring. (See Appendix 2 for technical drawing)

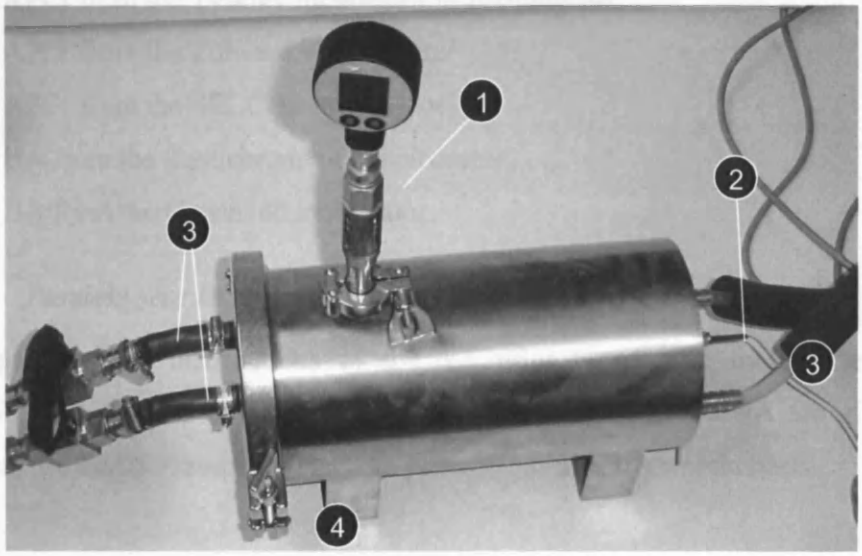

Figure 5-4 Reaction vessel

The receptacle for the solids is shown in Figure 5-5. It was made of stainless steel for effective heat transfer between the solid and the cooling plate. It was perforated (1) so that the temperature probe could measure the temperature, as close as possible to the reacting solid. The distance between the perforation and the base of the receptacle and the cooling plate is 2mm.

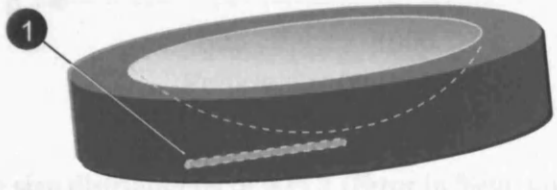

Figure 5-5 Ash holder

The relative humidity in the vessel is controlled by placing a 100ml crystallising basin inside the chamber containing either water (for a relative humidity of 100%) or a saturated salt solution. Saturated solutions of NaCl and $Na_2Cr_2O_7 \cdot 2H_2O$ were used to control the relative humidity at levels of 65% and 45% respectively.

5.4 Characterisation of the Ash

BA and APCr from different incinerators across the UK were supplied by Ballast Phoenix Ltd. and Onyx and were subjected to accelerated carbonation. The ashes provided were:

- APCr from the Tyseley incinerator in Birmingham
- APCr from the Edmonton incinerator
- APCr from the SELCHP incinerator
- BA from the Castlebromwich incinerator
- BA from the Cleveland incinerator

5.4.1 Particle size Distribution

The particle size distributions of the ash prior to reaction for Tyseley and Edmonton APCr and those for Castlebromwich and Cleveland BA are given in Figures 5-6 and 5-7, respectively. The percentages are on a weight basis.

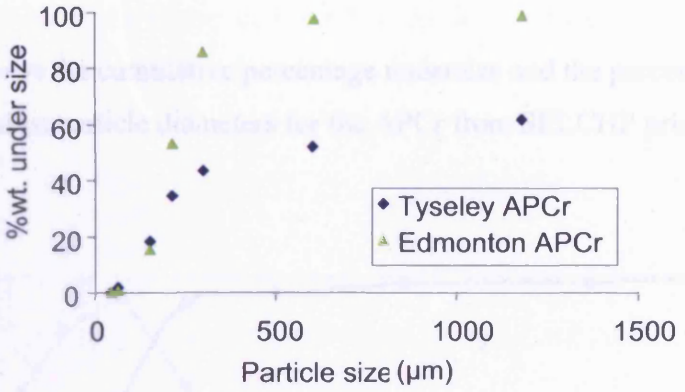

Figure 5-6 Particle size distributions of APCr (Error in %wt. under size= ± 3%)

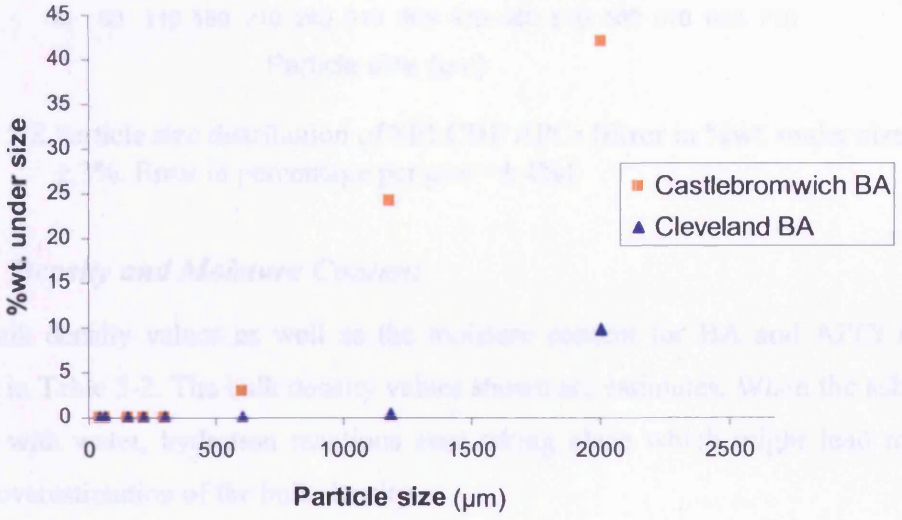

Figure 5-7 Particle size distributions of BA (Error in %wt. under size= ± 3%)

Table 5-1 shows the average particle size for the BA and the APCr.

Ash	Average particle size (µm)
Tyseley APCr	918 ± 40
Edmonton APCr	156 ± 6
SELCHP APCr	66 ± 3
Castlebromwich BA	1580 ± 60
Cleveland BA	2090 ± 80

Table 5-1 Average particle size of BA and APCr

Figure 5-8 shows the cumulative percentage undersize and the percentage frequency against particle diameters for the APCr from SELCHP prior to carbonation.

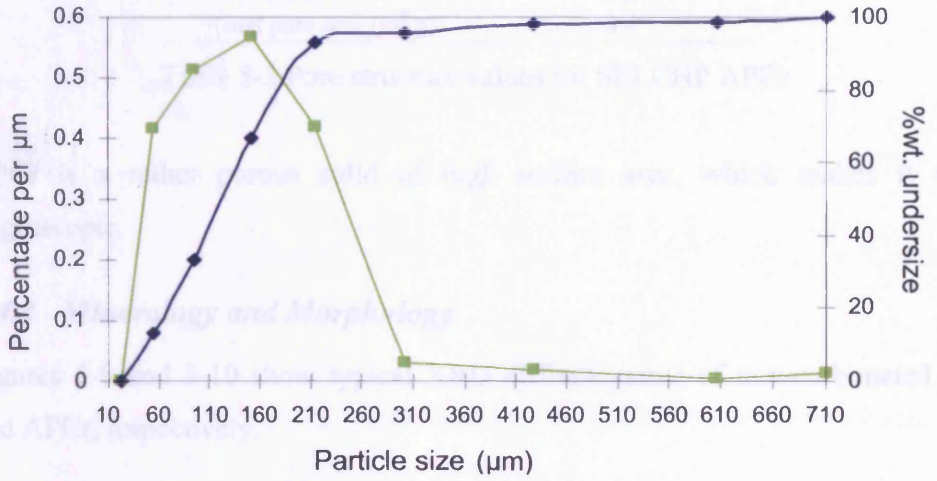

Figure 5-8 Particle size distribution of SELCHP APCr (Error in %wt. under size= ± 3%. Error in percentage per µm = ± 4%)

5.4.2 Density and Moisture Content

The bulk density values as well as the moisture content for BA and APCr are shown in Table 5-2. The bulk density values shown are estimates. When the ash is mixed with water, hydration reactions start taking place which might lead to a slight overestimation of the bulk density.

Ash	Moisture content (%)	Density (kg/m^3)
Tyseley APCr	2.50 ± 0.03	423 ± 4
Edmonton APCr	1.200 ± 0.006	683 ± 7
SELCHP APCr	2.900 ± 0.015	563 ± 6
Castlebromwich BA	16.8 ± 1.3	1031 ± 10
Cleveland BA	22 ± 2	1248 ± 12

Table 5-2 Bulk density and moisture content of BA and APCr

5.4.3 Pore Structure

When dealing with porous solids, it is very important to characterise the size and distribution of the pores, as the rate of carbonation is partly controlled by the diffusion characteristics of the pore structure (see section 2.3.4). The measured

values of porosity, tortuosity and total pore area for APCr from SELCHP incinerator are showed in Table 5-3.

Physical property	SELCHP APCr
Porosity (%)	73
Tortuosity	6.2
Total pore area (m^2/g)	4.4

Table 5-3 Pore structure values for SELCHP APCr

APCr is a rather porous solid of high surface area, which makes it very hygroscopic.

5.4.4 Mineralogy and Morphology

Figures 5-9 and 5-10 show typical XRD diffractograms of non-carbonated BA and APCr, respectively.

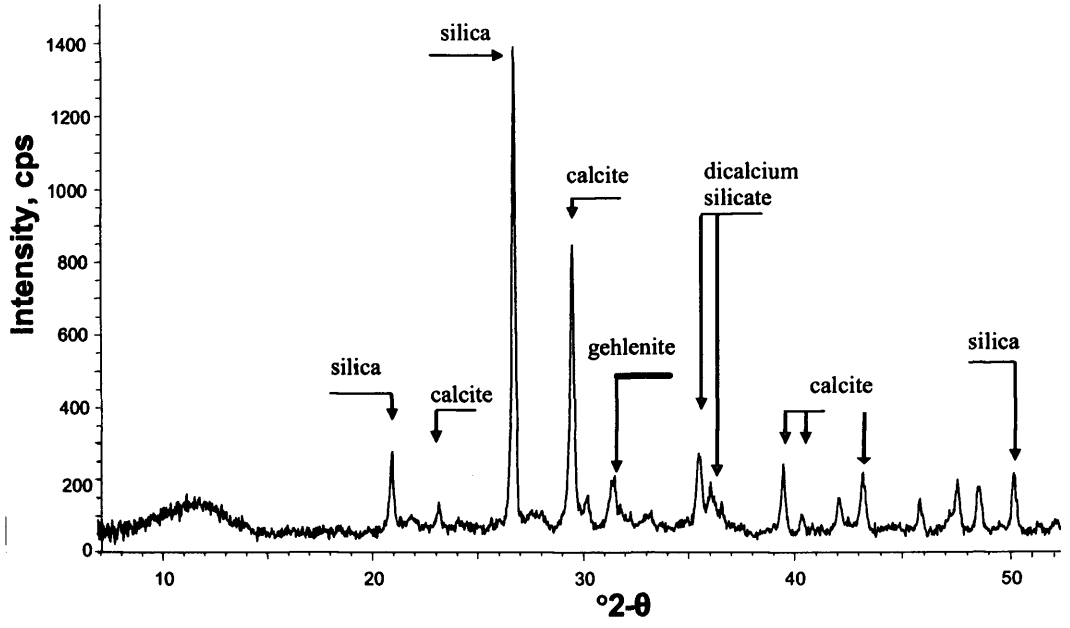

Figure 5-9 XRD Diffractogram of Castlebromwich BA before carbonation

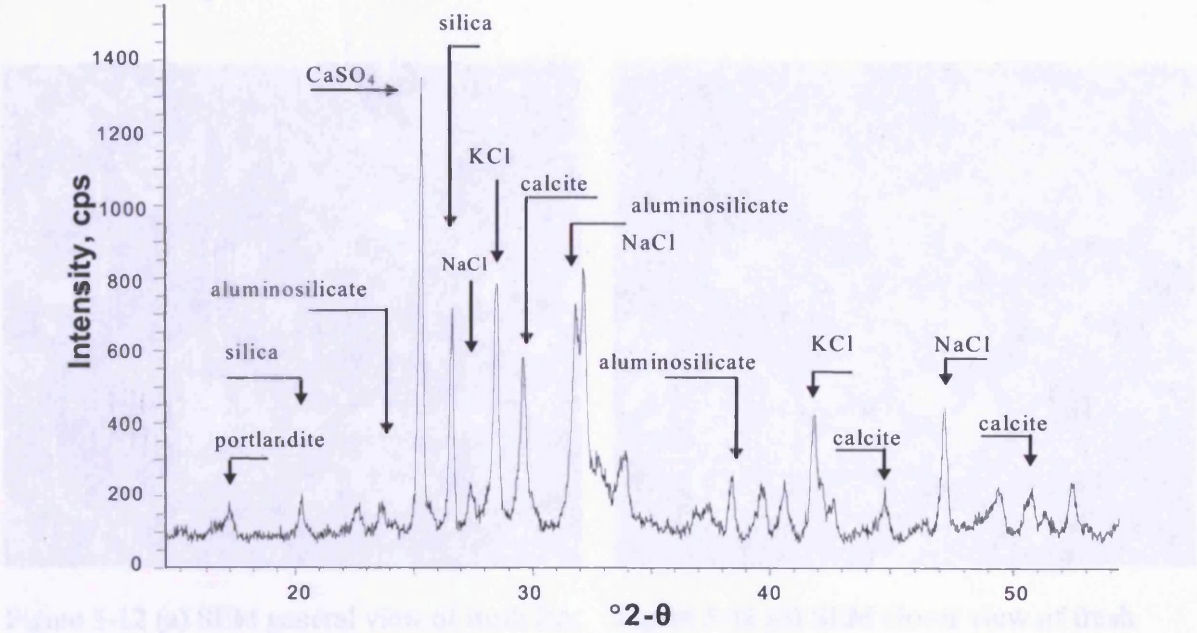

Figure 5-10 XRD Diffractogram of Edmonton APCr before carbonation

The morphology of MSWIr was determined using a Scanning Electron Microscope (SEM). Figures 5-11 and 5-12 show the characteristic morphology of APCr and BA particles, respectively, at different magnifications.

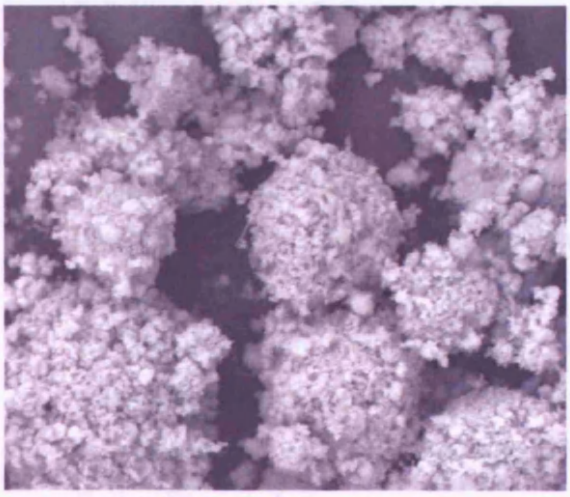

Figure 5-11 (a) SEM general view of fresh APCr, magnification x500

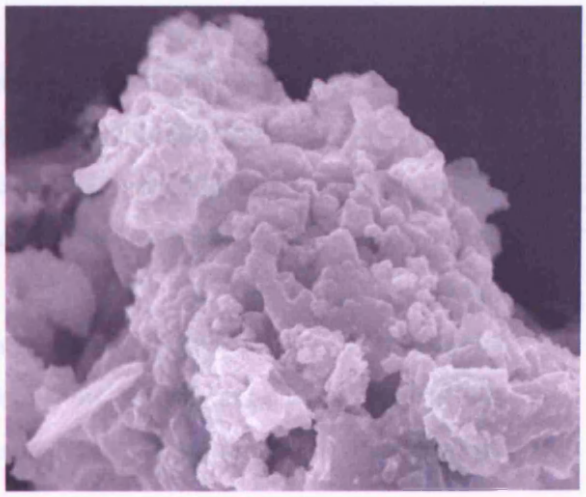

Figure 5-11 (b) SEM closer view of fresh APCr, magnification x5000

The particles of APCr are very small, ranging from tens of micrometers to mm. They appear spherical and highly porous. The microtexture is granular (see Figure 5-11 (b)) and individual grains are clearly visible.

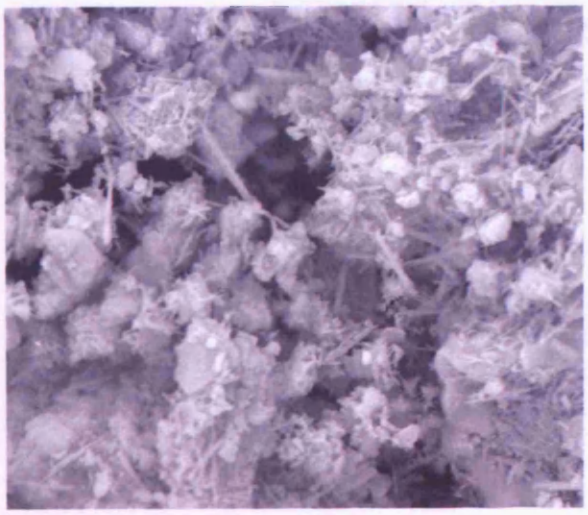

Figure 5-12 (a) SEM general view of fresh BA, magnification x1000

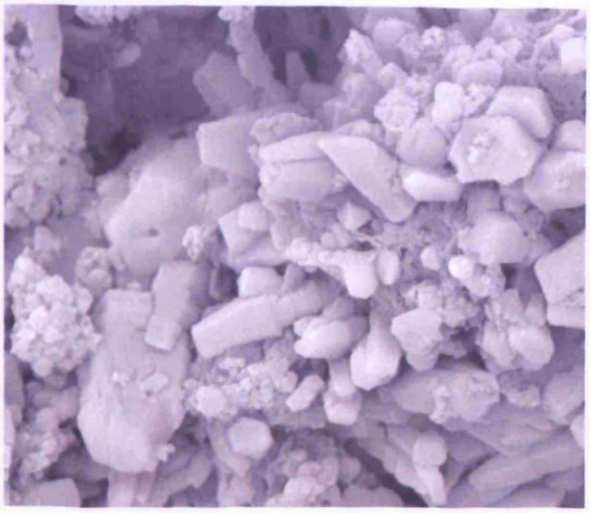

Figure 5-12 (b) SEM closer view of fresh BA, magnification x5000

The BA appears as irregularly formed lumps. The grain size ranges from micrometres to cm. The microtexture is porous and facetted crystalline parts can be observed. The single crystals present a fibrous, ribbon-like or tabular shape (see Figure 5-12 (a)).

5.4.5 Chemical Characterisation

The chemical characteristics of incineration residues are the major reason for concern over their environmental impacts and ultimate management. MSWIr contain alumina, silica, iron oxide, calcium oxide and other metal oxides which lead to a high pH material and risk of heavy metals leaching.

APCr contain more dioxins and heavy metals than BA, especially volatile metal compounds and soluble salts. Table 5-4 shows the typical range of concentrations of major oxides and minor metals in BA and APCr. These data were provided by Ballast Phoenix Ltd.

	Castlebromwich BA	Tyseley APCr
Major Oxides (%w.)		
CaO	12 - 18	17 - 27
SiO_2	47 - 60	15 - 27
Al_2O_3	7 - 15	8 - 16
P_2O_5	1.5 - 2	1 – 2.5
K_2O	1 - 2	4 – 10
TiO_2	0.5 - 2	1 - 2.5
MnO	0.08 - 0.12	0.1 -0.25
Fe_2O_3	10 - 20	1 - 3
MnO_2	0.1 - 0.3	
MgO	1.5 - 4	1.5 – 3
Na_2O	3 - 8	5 - 8
SO_4	1 - 1.5	7 - 10
Cl	0.1 - 0.3	6 - 8
Minor metals (mg/kg)		
Cr	100-120	180-200
Zn	-	75-80
Pb	5150-5200	2300-2500
Ni	100-110	4-7
Cu	2010-2060	750-780
As	80-100	8-12
Cd	20-25	0.5-2
Hg	0.2-0.4	0.4-0.6

Table 5-4 Chemical Analysis of BA and APCr (provided by Ballast Phoenix Ltd.)

The chemical composition of APCr from SELCHP, as analysed by XRF, is shown in Table 5-5.

Oxide composition	Mass fraction (%)	s.d.	Element	Content (ppm)	s.d.
SiO_2	30.00	0.14	Zn	7520.58	4
Na_2O	7.81	0.01	Pb	3025.54	3
Al_2O_3	12.12	0.11	Br	2061.60	2
MgO	2.50	0.01	Cu	534.36	4
Fe_2O_3	1.05	0.01	Sr	473.98	3
MnO	0.04	0.01	Ba	319.46	80
TiO_2	0.53	0.01	As	210.66	2
CaO	36.27	0.12	Zr	111.34	7
K_2O	2.03	0.01	Ni	70.32	4
SO_3	6.29	0.01	Ce	58.90	31
			W	53.88	4
			La	45.04	8
			Rb	23.80	1
			Ga	21.56	1
			Co	14.16	2
			Th	11.58	2
			Y	4.86	5
			Nb	2.16	2
			Mo	0.94	1
			Bi	0.86	1
			Se	0.04	1

Table 5-5 Chemical composition of APCr from SELCHP incinerator.

5.5 Experimental Methods

The ashes were received damp and were dried at 105°C in an oven to constant weight prior to investigation. They were characterised for their moisture content, bulk density, particle size distribution and mineral phases (using XRD), whilst their morphology was studied using the SEM, as described in the previous sections. The ashes were stored in air tight containers. The samples from SELCHP incinerator were received every three months to ensure the freshness of the APCr.

5.5.1 Determination of Optimum Reaction Conditions

To ascertain their susceptibility to accelerated carbonation and to determine the optimum range of particle size, water content and reaction time the ashes were carbonated in the stainless steel chambers (see Figure 5-1) exposing the ash to a 100% CO_2 atmosphere at 65% relative humidity and at a pressure of 3 bars. The conditions in the chambers were kept constant for all the experiments. Each experiment was repeated 3 times and an average value was taken.

Before exposing the ashes to CO_2, they were mixed thoroughly with water in 100ml beakers at selected water-to-solid (w/s) ratio. Then the mixed samples were placed in 9ml cylindrical plastic moulds of 25 mm internal diameter. For each set of experiments control samples were prepared in the same manner, sealed and stored under ambient laboratory conditions for the same time period.

Before starting the reaction, the chambers were flushed with CO_2 three times to ensure there was no air left inside. The extent of the reaction of the ash with the CO_2 was assessed by the gain in weight between the initial dry powder and the dried product, being proportional to the amount of CO_2 that had combined with the sample. This value was compared to the weight gain experienced by the control sample. The resulting value indicates the CO_2 that has reacted with the material. The ashes were dried before and after carbonation in an oven at 105° until constant weight.

Reaction time: The ashes were mixed with water at a ratio of 0.2 which is known to be optimum for carbonation of cement solidified wastes (see section 2.3.4). The samples were exposed to CO_2 for different time intervals from 20 min to 24 hours and the extent of reaction was evaluated for each set of experiments.

Size fraction: Four different size fractions were separated by sieving for two of the APCr and the BA samples, which were ground prior to sieving. Table 5-6 shows the different fractions into which they were separated. Then, once mixed with the water, they were left to carbonate for the time determined in the first set of experiments (3 hours).

Tyseley APCr	Edmonton APCr	Cleveland and Castlebromwich BA
d < 75 μm	d < 125 μm	d < 500 μm
75 μm < d < 125 μm	125 μm < d < 212 μm	500 μm < d < 710 μm
125 μm < d < 212 μm	212 μm < d < 500 μm	710 μm < d < 2800 μm
d>212 μm	d > 500 μm	d > 2800 μm

Table 5-6 Selected size fractions of APCr and BA to determine the optimum size fraction (where d is the diameter)

Water-to-solid ratio: For the optimum water content, samples of BA and APCr residues of the selected size fraction (d < 710 μm and d <212 μm respectively) were carbonated in the same chamber, during the same time interval, at different water-solid ratios ranging between 0 and 0.6.

5.5.2 Kinetic Experiments

The experiments to ascertain the kinetics of carbonation are carried out in the rig shown in Figure 5-3 using APCr from SELCHP incinerator. To ensure the conditions previously determined were still optimum in the new system, the same set of experiments was completed in the new rig. These conditions were then kept constant for all the kinetic experiments. However, the fraction below 212 μm was not separated, as more than 95% of this APCr was below that size (see Figure 5-6).

The experimental procedure followed was fundamentally the same as explained above for the chambers. The ashes were mixed with the selected amount of water and then placed in the holder in a uniform layer of 3 mm. The reactor was closed tightly, flushed three times with CO_2 and filled to a pressure of 3 bars with the nitrogen/CO_2 mixture. The drop in the pressure and the temperature were recorded throughout the reaction. The pressure drop indicated the CO_2 being consumed by the carbonation reaction. The experiments were replicated 3 times.

5.5.2.1 Controlling Mechanism

To be able to determine the kinetic model of carbonation it is important to know the controlling mechanism. To ascertain this mechanism APCr from the SELCHP incinerator was carbonated using the rig showed in Figure 5-3.

For this set of experiments, the conditions of reaction were kept constant at their optimum value (t = 3h, w/s = 0.3 and 100% CO_2). The variables that were changed to ascertain their influence on the mechanism of reaction were:

- the amount of ash
- the particle size
- the arrangement of the system

5.5.2.2 Kinetic Model

The determination of the kinetic model that best describes the carbonation of MSWIr required two different kinds of experiment. The first involved varying the concentration of the main reactants (water and CO_2) whilst keeping the temperature constant (at 23°C) to determine the rate equation. In the second, the concentrations were kept constant for different temperatures; 50% was the selected CO_2 concentration and 0.3 was the selected w/s ratio for this second set of experiments. The selected values of CO_2 concentration, water-to-solid ratio and temperature were the optimum values for carbonation.

Table 5-7 shows the range of concentrations for water and CO_2 and the temperature range selected for the kinetic experiments.

Variable	Interval
$[CO_2]$	10% - 100%
w/s ratio	0.2 – 0.6
T	10°C – 80°C

Table 5-7 Variables range for kinetic experiments

The CO_2 concentration in the reactor was adjusted by dilution with nitrogen to a pressure of up to 3 bars, as explained above. The water-to-solid ratio was varied when preparing the initial mixture. The temperature was kept constant by fixing the selected value on the temperature controller. These experiments were carried out at 65%, 45% and uncontrolled relative humidity (5-20%).

5.5.2.3 Influence of particle size on kinetics

A further set of experiments was carried out to determine the influence of particle size on the reaction kinetics. The APCr were separated into three size fractions prior to drying:

- 0 μm <d < 45 μm
- 45 μm < d < 90 μm
- 90 μm < d

The experiments were then carried out as described in section 5.5.2.2. Each of the fractions was characterised using XRD before and after carbonation.

5.5.3 Analytical Characterisation

To characterise the differences in mineralogy and microstructure of the ash after carbonation, the ash samples were analysed by means of XRD and SEM respectively before and after carbonation. The carbonate content was ascertained using DTA. For the three different analysis the ashes were previously dried to constant weight at 105°C and ground to a particle size < 20 μm.

CHAPTER 6

6 Results and Discussion

6.1 Introduction

In this Chapter the experimental results to optimise and model the accelerated carbonation of APCr are shown and discussed. The work reported in this Chapter can be divided into three stages.

In the first stage, the fundamental variables determining the extent of carbonation were selected, based on their influence on the diffusivity and reactivity of CO_2 (see section 2.3.4). These were subsequently evaluated and the optimum values ascertained both for BA and APCr. The major physical and chemical changes in APCr and BA after carbonation were also discussed. This is reported in section 6.2.

The second stage focused on the kinetic modelling of APCr. APCr were selected based on the higher extent of carbonation achieved than for BA. The first step to kinetic modelling involved the determination of the mechanism controlling the rate of reaction. Then, the mathematical expression describing the experimental data was derived, in terms of a kinetic triplet and a reaction mechanism was drawn. The validity of the model was verified by various analytical techniques. This is reported in section 6.3.

The third stage involved the evaluation of the influence of particle size on the kinetics of carbonation. APCr were divided into three different size fractions and the optimum conditions for carbonation, the best kinetic fit and the extent of carbonation, were evaluated for each fraction. The carbonation experiments for this section were carried out by Sun Jia, an MSc student under my supervision. I designed and directed the experimental programme. The discussion of the experimental results is supported by the analysis of the mineralogical changes in the different fractions. This is reported in section 6.4.

6.2 Optimum Conditions for Carbonation

6.2.1 Reaction Time

The CO_2 uptake with time for Edmonton APCr and Cleveland BA are given in Figures 6-1 and 6-2 respectively. As described in 5.5.1, the experiments were carried out at 3 bar, 65% RH, w/s = 0.3 and 100% CO_2. The conditions in the chambers were kept constant for all the experiments.

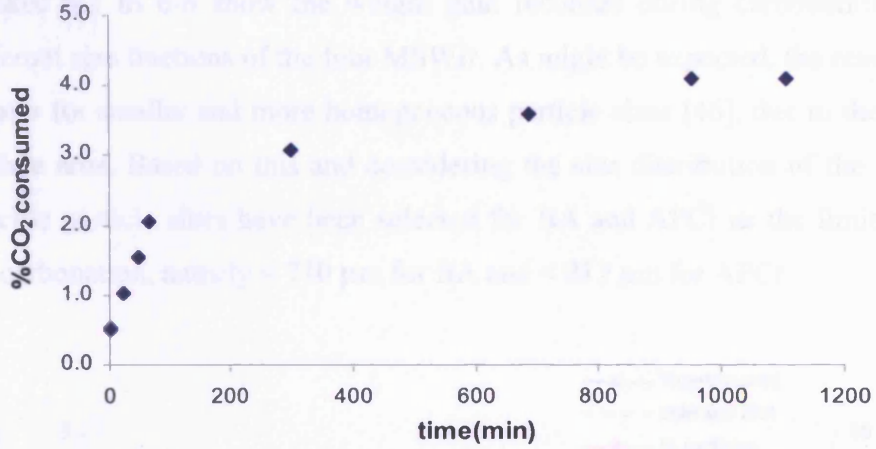

Figure 6-1 Percentage of CO_2 consumed with time by Edmonton APCr. (Error in $\%CO_2$ uptake = ± 0.5 %)

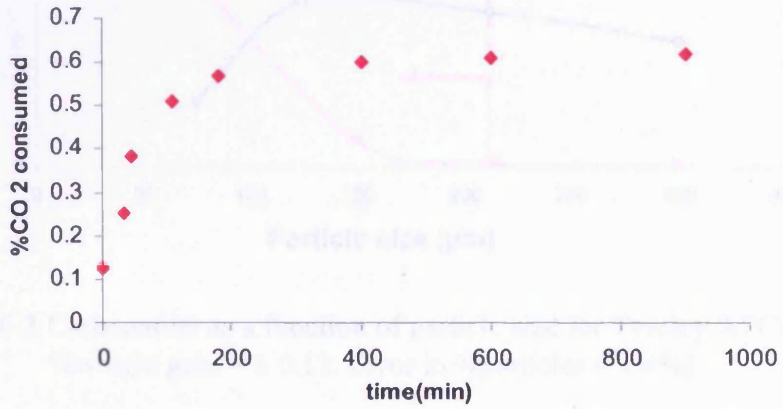

Figure 6-2 Percentage of CO_2 consumed with time by Cleveland BA. (Error in $\%CO_2$ uptake = ± 0.5 %)

Initially there was a steep rise in the consumption of the gas, which then slowed down until the sample was saturated. A compromise is required between the reaction time and the extent of reaction. When carbonating the ash for 24 hours, 75% of the reaction took place in the first 150 min. Therefore, 2.5 hours was selected as an optimum reaction time. For both APCr and BA, the velocity of consumption of CO_2 after 2.5 hours was rather slow.

As seen on the graphs, the consumption of CO_2 was higher for APCr than for BA. This is mainly due to the higher content of lime in APCr (see Table 5-4), although some of the physical characteristics also play an important role. APCr particles are of much smaller size and therefore the surface area of this ash is higher than that of BA, as is also the microporosity, factors that favour carbonation.

6.2.2 Particle Size

Figures 6-3 to 6-6 show the weight gain recorded during carbonation for the different size fractions of the four MSWIr. As might be expected, the reaction was greater for smaller and more homogeneous particle sizes [46], due to their higher surface area. Based on this and considering the size distribution of the particles, specific particle sizes have been selected for BA and APCr as the limiting sizes for carbonation, namely < 710 μm for BA and < 212 μm for APCr.

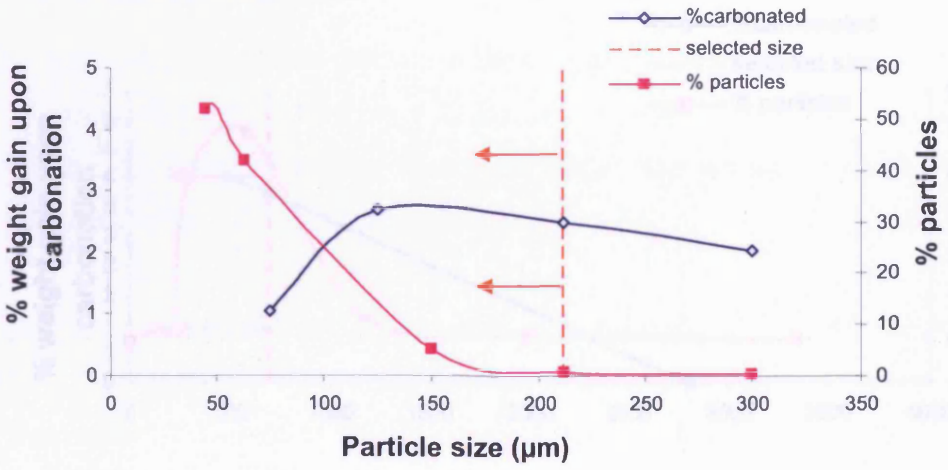

Figure 6-3 Carbonation as a function of particle size for Tyseley APCr. (Error in %weight gain = ± 0.12. Error in %particles = ± 4%)

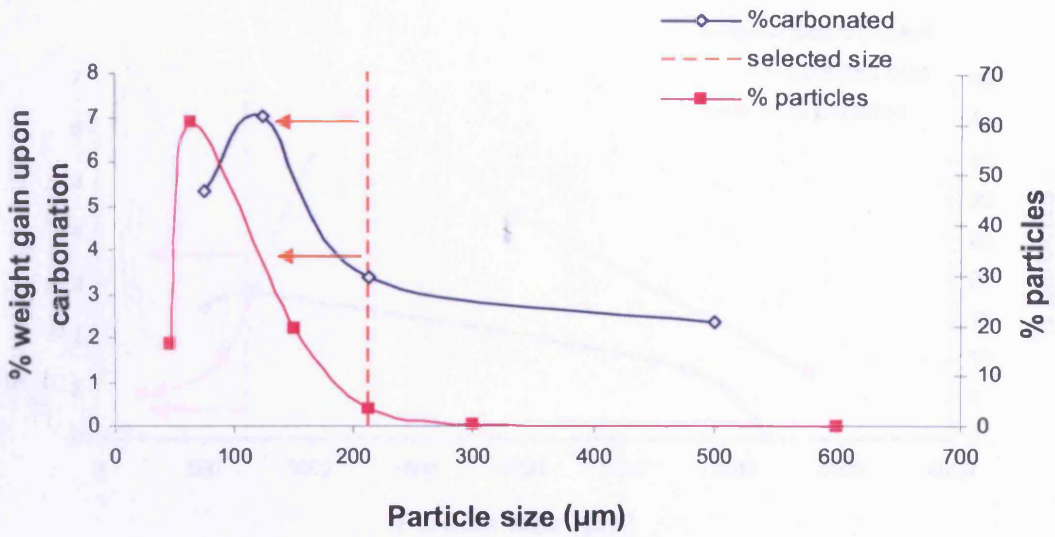

Figure 6-4 Carbonation as a function of particle size for Edmonton APCr. (Error in %weight gain = ± 0.12. Error in %particles = ± 4%)

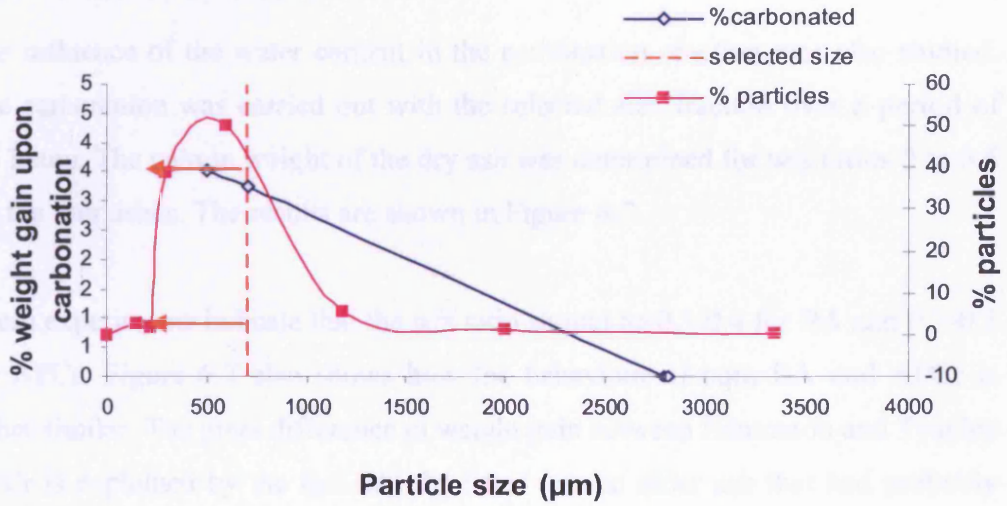

Figure 6-5 Carbonation as a function of particle size for Castlebromwich BA. (Error in %weight gain = ± 0.12. Error in %particles = ± 4%)

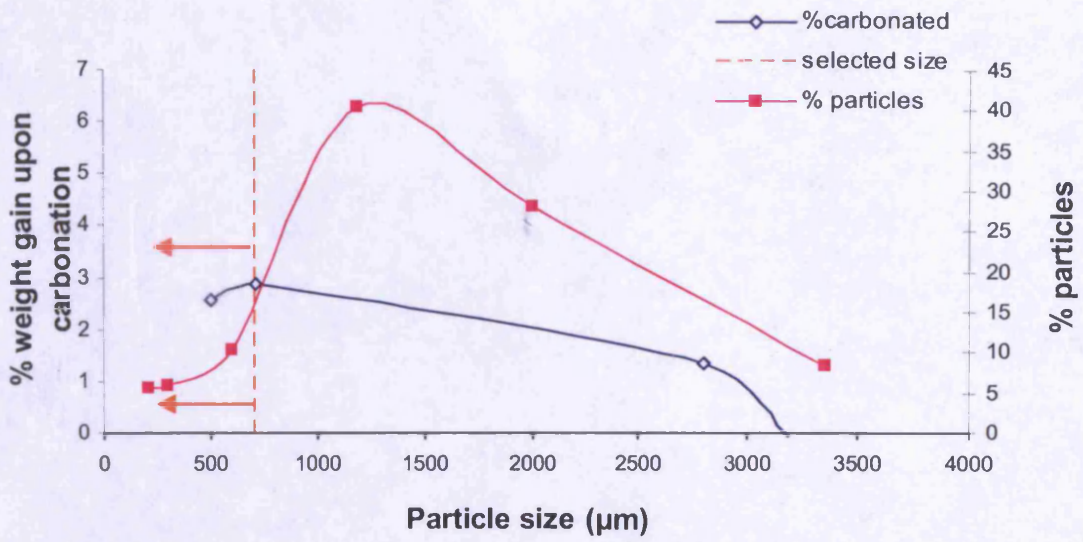

Figure 6-6 Carbonation as a function of particle size for Cleveland BA. (Error in %weight gain = ± 0.12. Error of %particles = ± 4%)

6.2.3 Water-to-solid ratio

The influence of the water content in the carbonation reaction was also studied. The carbonation was carried out with the selected size fraction over a period of 2.5 hours. The gain in weight of the dry ash was determined for w/s ratios 0 to 0.6 for the four ashes. The results are shown in Figure 6-7.

These experiments indicate that the w/s ratio should be 0.3-0.4 for BA and 0.2-0.3 for APCr. Figure 6-7 also shows how the behaviour of both BA and APCr is rather similar. The great difference in weight gain between Edmonton and Tyseley APCr is explained by the fact that the latter was an older ash that had probably already undergone natural carbonation to a considerable extent.

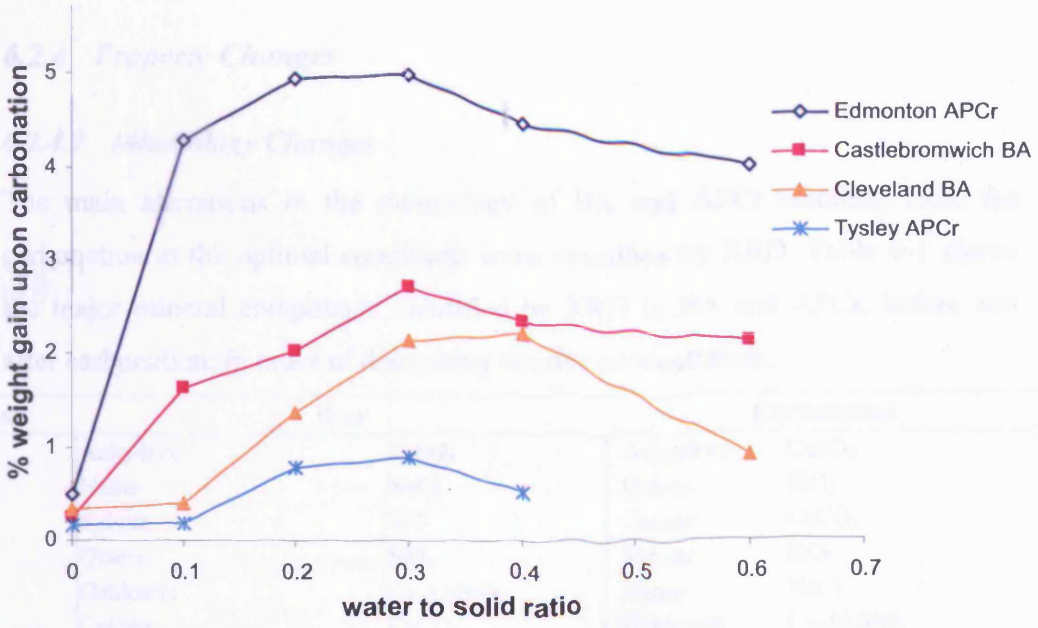

Figure 6-7 Carbonation as a function of the water-to-solid ratio for the four MSWIr. (Error in %weight gain = ± 0.12)

It is known that water is necessary for the carbonation reaction to proceed, but too much water hinders the diffusion of CO_2 into the pores of a solid. Pore water hydrates and solvates the CO_2 and dissolves the Ca^{2+} ions from the solid phase to react and form $CaCO_3$. At low w/s ratios, the material's gas permeability is increased and the CO_2 effectively diffuses into the solid. Some authors have found the optimum ratio between w/s 0.06 and 0.20 [23, 44, 45], although others have successfully carbonated with values up to 0.35 [39].

6.2.4 Property Changes

6.2.4.1 Mineralogy Changes

The main alterations in the mineralogy of BA and APCr resulting from the carbonation at the optimal conditions were examined by XRD. Table 6-1 shows the major mineral compounds identified by XRD in BA and APCr, before and after carbonation, in order of decreasing relative concentration.

Ash	Raw		Carbonated	
APCr	Anhydrite	$CaSO_4$	Anhydrite	$CaSO_4$
	Halite	NaCl	Quartz	SiO_2
	Sylvite	KCl	Calcite	$CaCO_3$
	Quartz	SiO_2	Sylvite	KCl
	Gehlenite	$Ca_2Al_2SiO_7$	Halite	NaCl
	Calcite	$CaCO_3$	Gehlenite	$Ca_2Al_2SiO_7$
	Portlandite	$Ca(OH)_2$	Gibbsite	$Al(OH)_3$
	Thenardite	$NaSO_4$	Hematite	Fe_2O_3
	Na, K feldespar	$(AlSi_3O_8)Na, K$	Anhydrite	$CaSO_4$
	Sygenite	$K_2Ca(SO_4)_2H_2O$	Iron oxides and Hydroxides	
	Cementitious phases	CAS_2, AS	Calcium silicate complexes with metals	
	Complex oxides of metals (Pb, Cu, Ba, As, Zn)			
BA	Quartz	SiO_2	Quartz	SiO_2
	Calcite	$CaCO_3$	Calcite	$CaCO_3$
	Dicalcium silicate	C_2S	Gypsum	$CaSO_4 2H_2O$
	Hematite	Fe_2O_3	Gehlenite	$Ca_2Al_2SiO_7$
	Gehlenite	$Ca_2Al_2SiO_7$	Gibbsite	$Al(OH)_3$
	Olivine	$(Mg, Fe)_2SiO_4$	Calcium silicate complexes with metals	
	Wollastonite	$CaSiO_3$		
	Feldespar group	$(Al, Si)_4O_8(Ca,Na,K)$		
	Metal oxides and hydroxides (Pb, Zn, Cu, Cr, Ni, Mn, Fe, Mg)			

Table 6-1 Major compounds found in BA and APCr before and after carbonation

Figures 6-8 and 6-9 show the XRD diffractograms before and after carbonation, for Castlebromwich BA and Edmonton APCr, respectively. The ashes were fully carbonated for this analysis i.e. until there was no further uptake of CO_2, in order to better observe the property change.

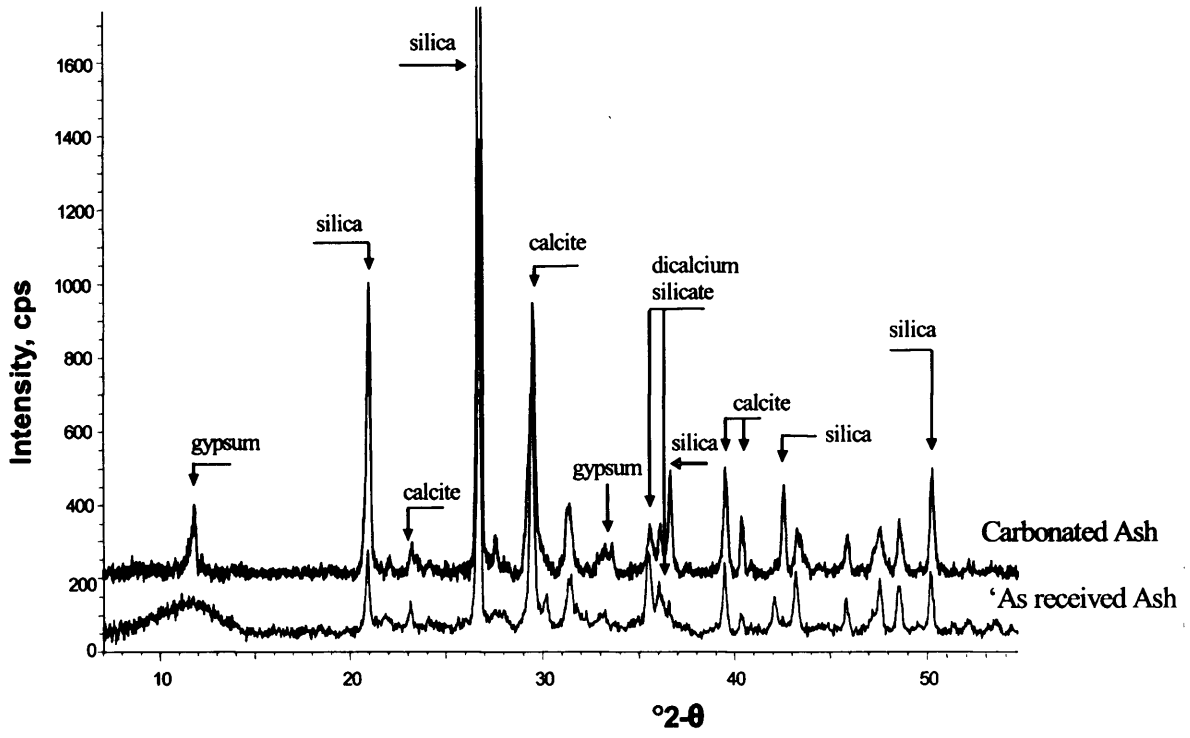

Figure 6-8 XRD Diffractograms of Castlebromwich BA

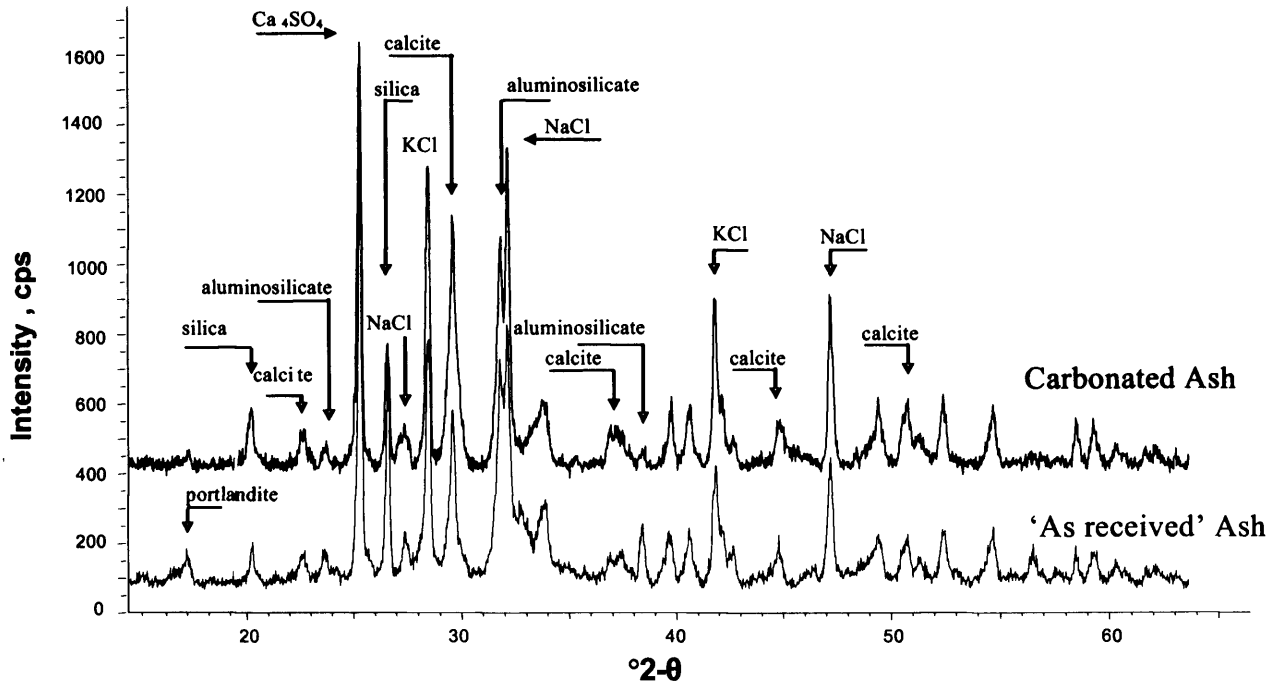

Figure 6-9 XRD Diffractograms of Edmonton APCr

The intensity of peaks corresponding to calcite and silica are higher in carbonated samples for both MSWIr. Both ashes have very noisy signals due to their heterogeneity and complex mineralogy. The presence of calcite in the initial samples can be attributed to partial, earlier weathering of the ash.

The breakdown of C_2S and the formation of calcite can be observed for BA. There was an increase in the degree of crystallinity in the diffractograms resulting from carbonation. In the non-carbonated sample of APCr there was some evidence of hydration by the existence of minor peaks for portlandite $Ca(OH)_2$, which was absent in the carbonated sample.

The XRD did not show peaks relevant to known heavy metal phases, which suggests that the detectable metals were present either as impure, complex compounds or as amorphous species [79]. The high content of chlorides in APCr can be explained as resulting from volatile metal chloride condensation due to flue gas temperature decrease downstream of the furnace [79].

6.2.4.2 Microstructure Changes

Examination of the ashes with a JEOL 5110 LV SEM, using both secondary electron and back-scattered imaging, revealed distinct differences in the morphology between carbonated and non-carbonated samples. Figures 6-10 (a) and (b) illustrate this by showing fracture surfaces of APCr from the SELCHP incinerator before and after carbonation, respectively. The appearance of the non-carbonated APCr is granular and individual grains are clearly visible. The carbonated sample reveals less porous solid where crystalline reaction products are clearly evident.

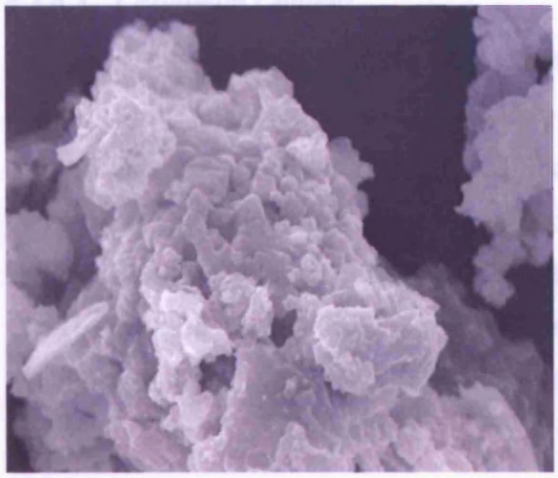

Figure 6-10 (a) Non-carbonated APCr

Figure 6-10 (b) Carbonated APCr

Figures 6-11 (a) and (b) show the images of BA from the SELCHP incinerator before and after carbonation, respectively. The difference in this case is less evident than for the APCr, as the extent of carbonation is lower for BA. Despite this, precipitated solids can be seen filling the pores of the ash.

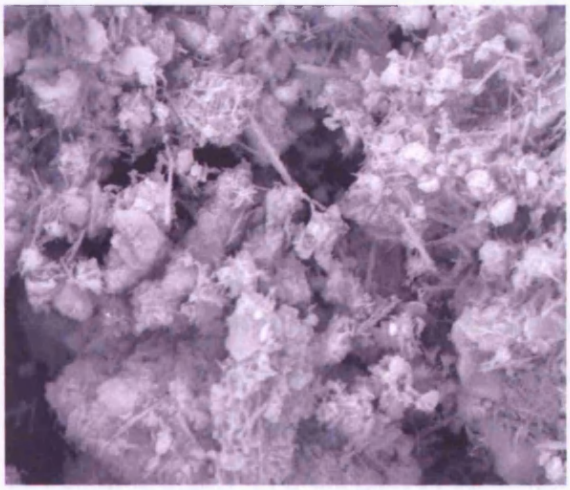

Figure 6-11 (a) Non-carbonated BA

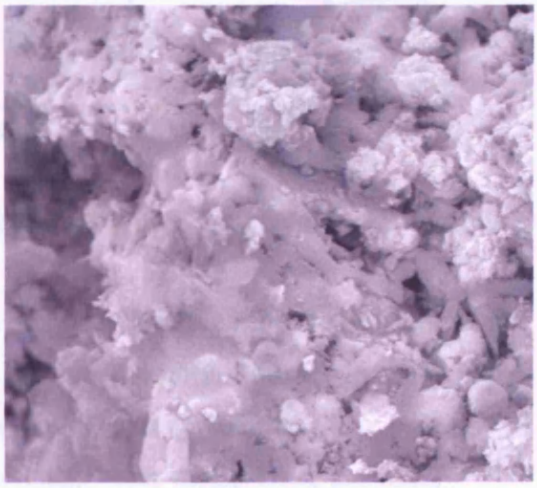

Figure 6-11 (b) Carbonated BA

6.2.4.3 Carbonate Content

The increase of carbonate content was determined by applying thermogravimetric and differential thermal analysis (TG/DTA). Figure 6-12 shows the weight loss and ΔT curve obtained with the DTA for carbonated APCr from the SELCHP incinerator. The weight loss curve indicates that in carbonated ash the loss of pore and combined water occurred below 200°C and the decomposition of the formed $CaCO_3$ occurred above 450°C. The combustion of organics is characterised by a positive peak in the ΔT curve at around 300°C.

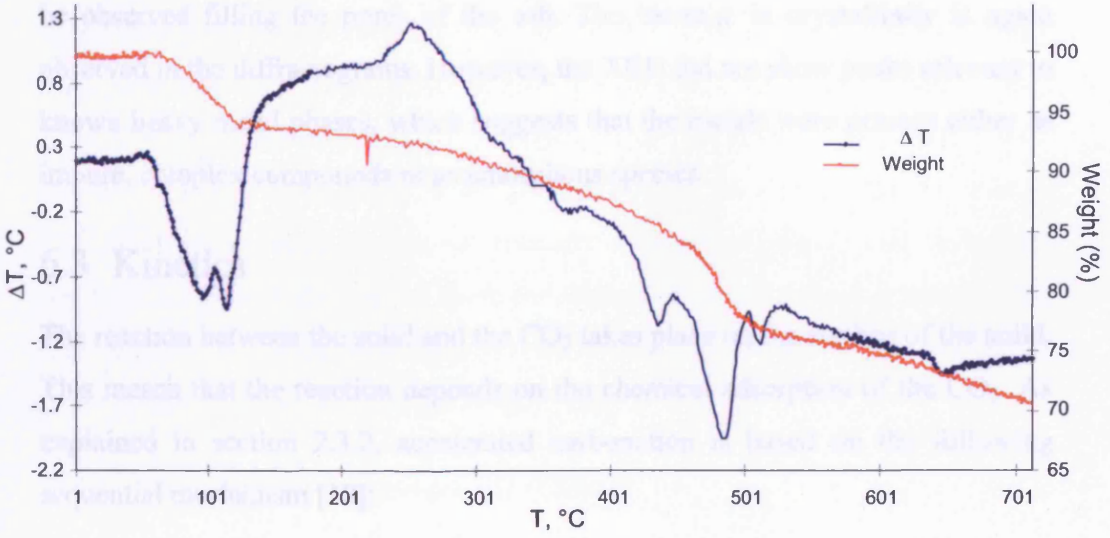

Figure 6-12 TG/DTA of SELCHP APCr

Table 6-2 shows the difference in carbonate content between the ashes before and after 24 h carbonation at 100% CO_2 and 65% relative humidity. These values are also compared with the gain in weight of the samples after carbonation. The gain in weight is higher than the gain in carbonate content. This means there are other reaction products being generated, as was qualitatively shown in the XRD analysis.

Kind of ash	% $CaCO_3$ before	% $CaCO_3$ after	$CaCO_3$ gain (%)	Weight gain (%)
BA	3.46 ± 0.13	4.74 ± 0.13	1.34 ± 0.14	3.19 ± 0.12
APCr	11.84 ± 0.13	16.01 ± 0.13	4.96 ± 0.07	7.31 ± 0.12

Table 6-2 Carbonate content and weight gain for BA and APCr

The gain in calcite is expressed as a function of the initial mass and is calculated as follows:

$$\%\,CaCO_3\ gain = \frac{(\%\,CaCO_3\ after - \%\,CaCO_3\ before)}{(1 - \%\,CaCO_3\ after)} \qquad (6.1)$$

6.2.4.4 Conclusion

Carbonation generates polymorphic $CaCO_3$, which physically encapsulates waste components. The carbonate coats the original grains of the powdered waste, generating a matrix thermodynamically stable and suited to the long-term encapsulation of toxic compounds. In the SEM crystalline reaction products can be observed filling the pores of the ash. The increase in crystallinity is again observed in the diffractograms. However, the XRD did not show peaks relevant to known heavy metal phases, which suggests that the metals were present either as impure, complex compounds or as amorphous species.

6.3 Kinetics

The reaction between the solid and the CO_2 takes place on the surface of the solid. This means that the reaction depends on the chemical adsorption of the CO_2. As explained in section 2.3.2, accelerated carbonation is based on the following sequential mechanism [38]:

1st. Diffusion of CO_2 in the gaseous layer surrounding the solid
2nd. Diffusion of CO_2 through the solid
3rd. Solvation of $CO_{2(g)}$ to $CO_{2(aq)}$
4th. Hydration of $CO_{2(aq)}$ to H_2CO_3
5th. Ionisation of H_2CO_3 to H^+, HCO_3^-, CO_3^{2-}
6th. Dissolution of calcium containing phases
7th. Nucleation of $CaCO_3$
8th. Precipitation of solid phases

Since these steps occur consecutively, if any one of them is slower than the others, that step becomes rate-determining. However, given the complexity of the waste materials, the reaction is likely to be influenced by more than one step.

When the APCr are in contact with water, the alkali chlorides, together with some calcium, magnesium, zinc, lead and cadmium salts, rapidly dissolve at first [81]. Since the concentration of calcium hydroxide is higher than the concentration of other hydration products, the reaction of CO_2 with $Ca(OH)_2$ predominates and the carbonation process can be simply described by the following overall reaction, which is the focus of this kinetic study:

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O \qquad (6.2)$$

This reaction represents only the final result of various steps through which the true reaction occurs. The second simplification is to consider the reaction (6.2) irreversible and instantaneous, so that the $CaCO_3$ precipitates immediately once the two reactants are together. If the pores are filled with water, the low rate of CO_2 diffusion in water hinders the reaction. However, if there is no water, the reaction does not occur. As in most heterogeneous non-catalytic processes, the rate of carbonation reaction varies considerably depending on the conditions under which the experiment is performed [103].

6.3.1 Verification of Optimum Conditions

As explained in section 5.5.2, to ensure that the same optimum conditions, determined using the carbonation chambers (Figure 5-1) still applied to the carbonation rig (Figure 5-3), the same sets of experiments were completed in the latter with the ash from the SELCHP incinerator. These conditions were then kept constant for the kinetic experiments. The kinetic study has been carried out only for SELCHP APCr. The influence of the particle size was not studied at this stage as 95% of the SELCHP APCr was below 212μm, the optimum limiting particle size determined previously.

6.3.1.1 Reaction Time

Figures 6-13 and 6-14 show the optimum reaction times. APCr and BA were left to react during 24 hours. When compared to the total CO_2 consumed, 75% and 79% of the gas was consumed in the first 3 hours for APCr and BA, respectively.

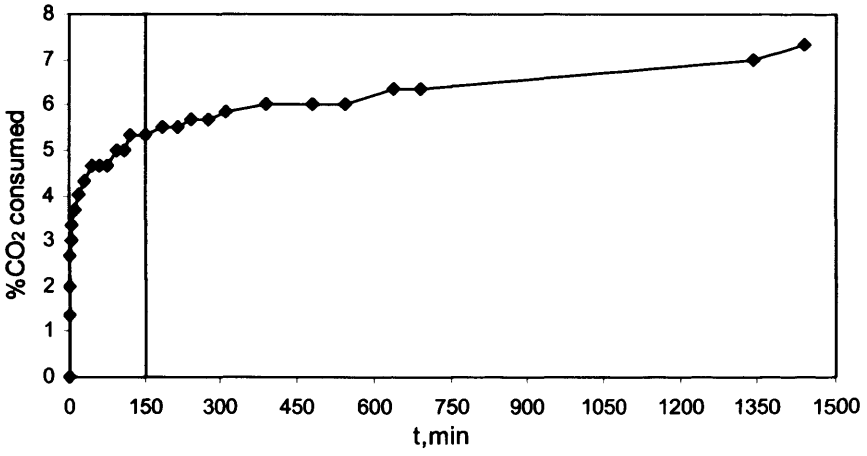

Figure 6-13 CO_2 consumed by SELCHP APCr. (Error in $\%CO_2$ consumed = ± 0.5)

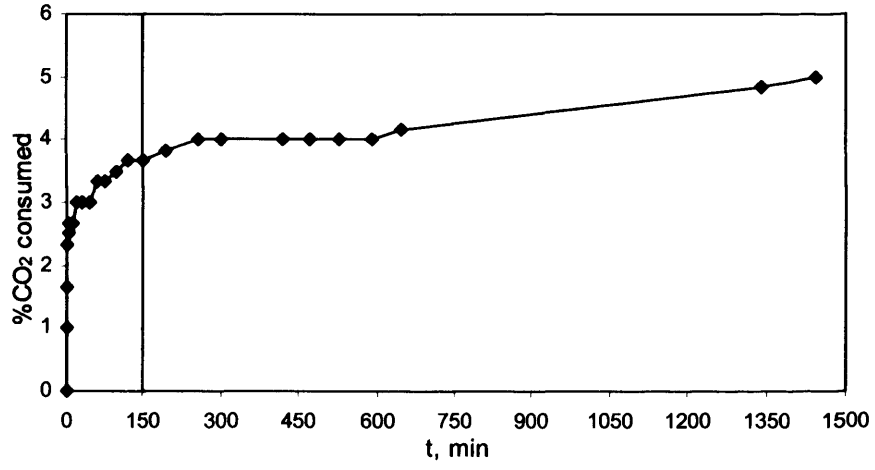

Figure 6-14 CO_2 consumed by SELCHP BA. (Error in $\%CO_2$ consumed = ± 0.5)

6.3.1.2 Water Content

Regarding the water content, Figures 6-15 and 6-16 show that in the same way as the previous system, w/s ratio of 0.3 gives an optimum extent of carbonation for both, BA and APCr.

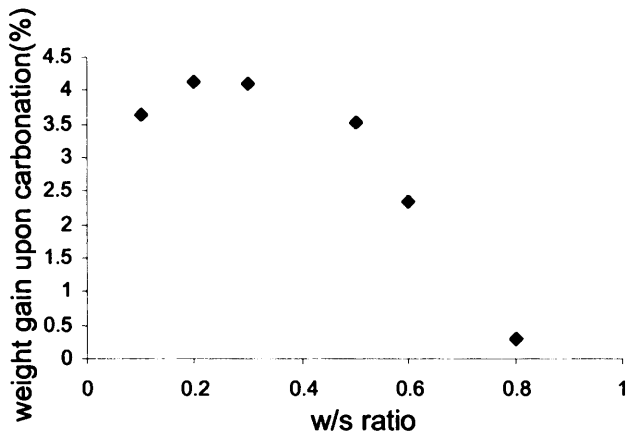

Figure 6-15 Carbonation as a function of w/s ratio for SELCHP BA. (Error in %weight gain = ± 0.12)

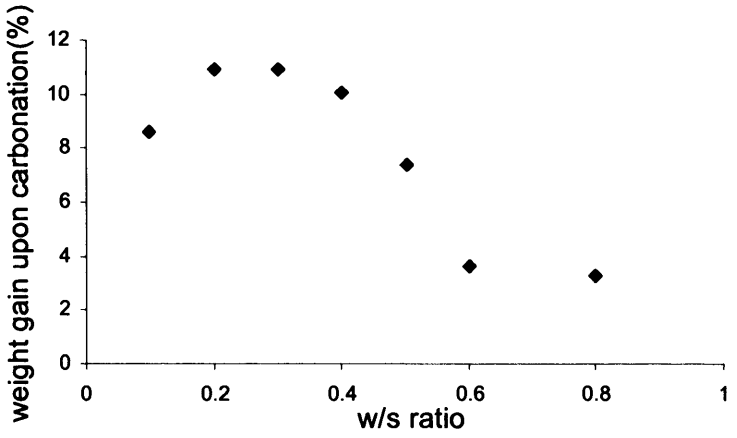

Figure 6-16 Carbonation as a function of w/s ratio for SELCHP APCr. (Error in %weight gain = ± 0.12)

6.3.2 Controlling Mechanism

The selected kinetic model for the accelerated carbonation of APCr is the shrinking core model. As explained in section 4.3 , for the case of porous particles this is a common behaviour if the resistance to reaction is much less than the resistance to diffusion of fluid reactant in the pores of the particle. The reaction occurs at first at the outer layers of the particle. Then the zone of reaction moves into the solid. At any time there is an unreacted core of material, which shrinks in size during the reaction.

The rate controlling steps of a fluid solid reaction are deduced by noting how the progressive conversion of particles is influenced by the operating conditions [101]. Figure 6-17 shows the evolution of the reaction with time and the comparison with the standard curves for the progressive conversion of spherical solids with chemical reaction, film diffusion, and diffusion through the layer of product control respectively. The comparison of kinetic runs with the predicted curves indicates the rate-controlling step. In Figure 6-17 x is the reaction conversion and τ is the time at complete conversion. 24h has been assumed as the time at complete conversion, as after that time the consumption of CO_2 is negligible (i.e. in the order of 10^{-4} moles/h). For this comparison the APCr particles have been assumed to be spherical.

The conversion was calculated as a function of the partial pressure of CO_2, as shown in equation (6.3).

$$x = \frac{V_{CO_2}}{R\,T\,n_{0CaO}}\left(P_{0CO_2} - P_{CO_2}\right) \qquad (6.3)$$

where n_{0CaO} is the initial number of moles of CaO in the APCr

V_{CO_2} is the effective volume of the reactor

R is the gas constant

T is the temperature in the reactor

P_{0CO_2} and P_{CO_2} are the partial pressures of CO_2 at time = 0 and at time = t, respectively.

When calculating the conversion, an induction period was taken into account. In the first few minutes after the system was closed, there were initial processes reducing the pressure before the reaction started. These include time for the sample to reach the selected reaction temperature, changes happening in the system when flushing the reactor (e.g. drop in relative humidity) and other slow processes preceding the main reaction.

As explained in section 5.5.2.1, for this set of experiments, the conditions of reaction were kept constant at their optimum value (t = 3h, w/s = 0.3 and 100% CO_2). The variables that were changed to ascertain their influence on the mechanism were: the amount of ash, the particle size and the arrangement of the system. Table 6-3 shows the different experiments that were run to ascertain the controlling mechanism.

Variable	Amount of ash (g)	Particle size	System arrangement
Experiment 1	15	Unclassified	Thick layer
Experiment 2	15	<100 µm	Thick layer
Experiment 3	15	Unclassified	3 mm layer
Experiment 4	7.5	Unclassified	Thick layer
Experiment 5	3.75	Unclassified	Thick layer

Table 6-3 Experimental set ups to ascertain the controlling mechanism

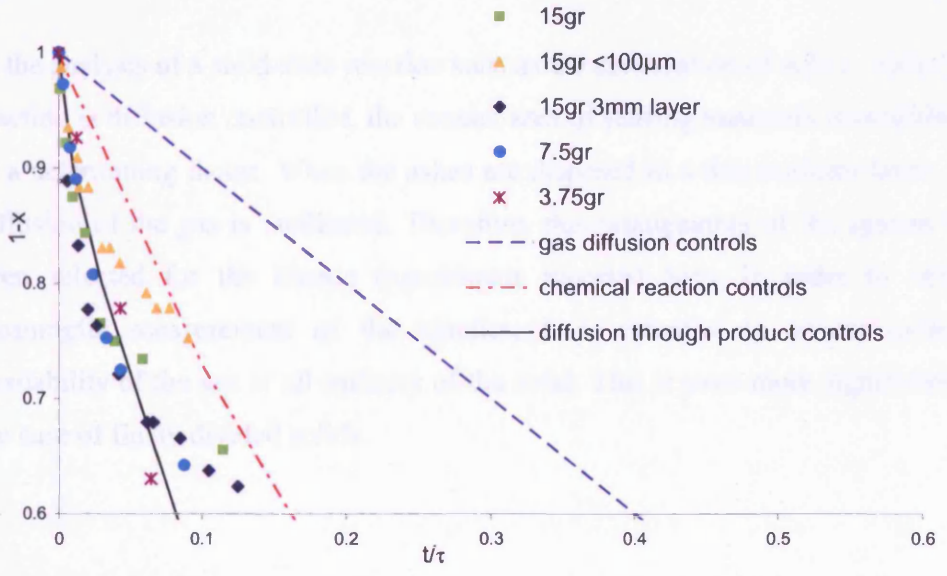

Figure 6-17 Progress of reaction with time for complete conversion for spherical particles. (Error in conversion = ± 0.014)

The results in Figure 6-17 show that the carbonation of APCr was diffusion-controlled, i.e. the slowest step was the diffusion of the gas to the solid reactant through the product layer, which agrees with previous studies of systems of similar nature [17, 42, 49, 92, 98, 116, 117]. Different experimental conditions were aimed at minimising the diffusion effect and for all experiments the reaction proved to be diffusion controlled.

It is known that the gas-solid reaction of a system such as pure CaO-CO_2 proceeds through two rate controlling step regimes. During the initial stages, the reaction occurs rapidly by heterogeneous surface chemical reaction kinetics. As $CaCO_3$ precipitates, the rate of reaction decreases due to the diffusion of reacting species through the product layer [98]. Given the partial carbonation and the complex nature of APCr, there is already a solid layer hindering the diffusion of CO_2 that made the reaction diffusion-controlled from the early stages.

The CO_2 and the interface of the unreacted core move inward towards the centre of the particle. However, the shrinkage of the unreacted core is slower than the flowrate of CO_2 to the core by a factor of about 100, which is roughly the ratio of densities of the carbonated APCr to the gas.

In the analysis of a solid-state reaction such as the carbonation of APCr, where the reaction is diffusion controlled, the contact area of starting materials is considered as a determining factor. When the ashes are disposed in a thin uniform layer, the diffusion of the gas is facilitated. Therefore, this arrangement of the system has been selected for the kinetic experiments reported here. In order to obtain meaningful measurement of the kinetics, it is essential to ensure uniform availability of the gas at all surfaces of the solid. This is even more significant in the case of finely divided solids.

6.3.3 Reaction Kinetics

Experimental measurements of reaction rates aim to determine the mechanism of a chemical change. A full kinetic analysis has at least three major stages:

I. Collection of experimental data

II. Computation of kinetic characteristics for the data from stage I

III. Evaluation of the significance of any parameters elucidated in stage II

This approach will help to predict behaviour under untested conditions from the results collected.

At stage II, a model-fitting approach was followed. The reliability of the model depends on the coherence between the kinetic model, the Arrhenius parameters and the kinetic scheme, calculated for the same reaction performed under both isothermal and non-isothermal conditions [107].

Carbonation proceeds along the following reaction steps:

$$Ca(OH)_2 \longrightarrow Ca^{2+} + OH^- \quad (6.4)$$

$$CO_{2\,(g)} \longrightarrow CO_{2\,(aq)} \quad (6.5)$$

$$CO_{2\,(aq)} + OH^- \longrightarrow HCO_3^- \quad (6.6)$$

$$CO_{2\,(aq)} + H_2O \longrightarrow H_2CO_3 \quad (6.7)$$

$$H_2CO_3 \leftrightarrow H\,CO_3^- + H^+ \leftrightarrow CO_3^{2-} + 2\,H^+ \quad (6.8)$$

$$Ca^{2+} + CO_3^{2-} \longrightarrow CaCO_3 \quad (6.9)$$

The amount of $CaCO_3$ that forms in a unit of time depends on the availability of $Ca(OH)_2$, the CO_2 concentration, the water content in the solid and the temperature. The effect of these factors on the kinetics of reaction is analysed individually in the following sections.

6.3.3.1 *Effect of CO_2 concentration*

The effect of gas phase CO_2 concentration on the carbonation reaction is shown in Figure 6-18 in terms of conversion vs. time t. After approximately 100 min, the reaction was close to completion and the final conversion was achieved in most cases after 150min. As can be seen from these plots the reaction did not achieve 100% conversion (i.e. complete conversion = 1).

As expected, the conversion of the reaction as well as the weight gain increased as the concentration of CO_2 was increased (see Table 6-4). However, the conversion achieved at 50% v/v CO_2 was only 5.1% lower than that achieved at 80% v/v CO_2 and 20% lower than that achieved at 100% CO_2. These are encouraging results when considering carrying out carbonation using flue gases, in which the CO_2 concentration is normally below 50% v/v CO_2. Therefore, when carbonating at a larger scale, the separation costs to increase the gas concentration on CO_2 would be reduced as 100% purity is not needed for an optimum carbonation.

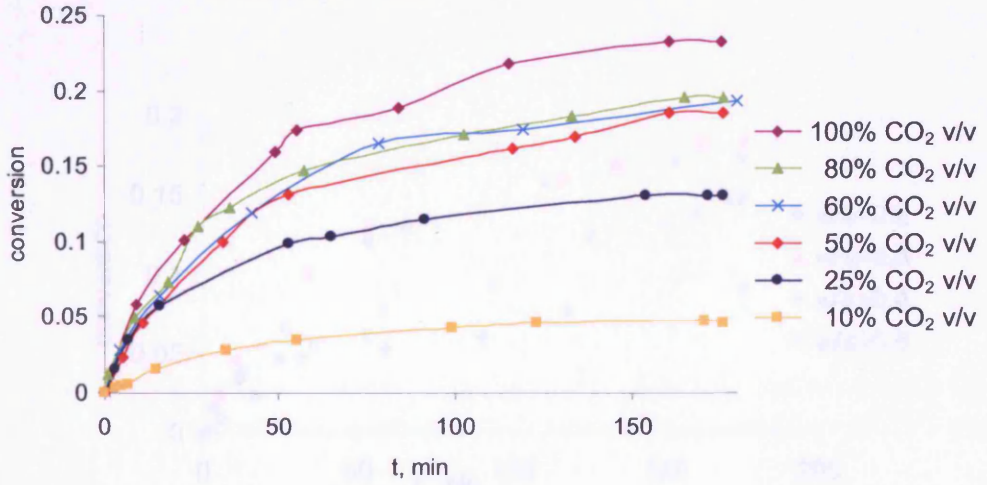

Figure 6-18 Evolution of reaction with time for different concentrations of CO_2. (Error in conversion = ± 0.014)

Table 6-4 shows the weight gain upon carbonation and the conversion achieved after carbonating the APCr for 3 hours at concentrations of CO_2 from 10 to 100%.

[CO2] (% v/v)	% Weight gain upon carbonation ± 0.12	Conversion ± 0.014
100	12.44	0.232
80	11.45	0.195
60	10.86	0.192
50	10.09	0.185
25	9.53	0.129
10	8.62	0.046

Table 6-4 Extent of carbonation at different concentrations of CO_2

6.3.3.2 Effect of water-to-solid ratio

The experiments showed that the lower the water-to-solid ratio, the higher the rate of reaction. This was due to the easier diffusion of CO_2 into the pores of the solid, as water was not blocking the pores. However, the final conversion achieved was lower, as shown in Table 6-5, due to the lower mobility of ions in the solid with reduced amounts of adsorbed water.

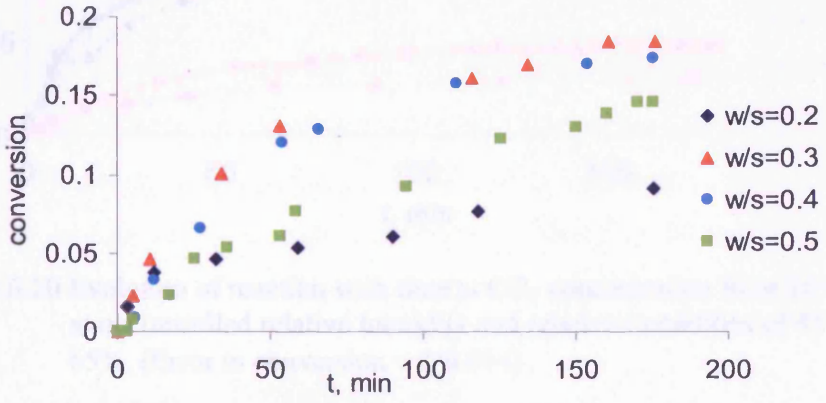

Figure 6-19 Evolution of reaction with time at water-to-solid ratio from 0.2 to 0.5. (Error in conversion = ± 0.014)

The lowest conversion was observed at a water-to-solid ratio of 0.2. The amount of water was too low for the reaction to proceed. The highest conversion was achieved at a water-to-solid ratio of 0.3. However, the highest weight gain was reached at a water-to-solid ratio of 0.4.

w/s	% Weight gain upon carbonation ± 0.12	Conversion ± 0.014
0.2	9.91	0.076
0.3	10.09	0.185
0.4	10.47	0.173
0.5	7.79	0.145

Table 6-5 Extent of carbonation at different water-to-solid ratios

6.3.3.3 Effect of relative humidity

The effect of relative humidity on the carbonation of APCr can be seen in Figure 6-20. At CO_2 concentrations ranging from 10% to 50%, the evolution of reaction with time did not vary much with the change in relative humidity. Thus, the reaction was of the zero order with respect to relative humidity in the concentration range examined.

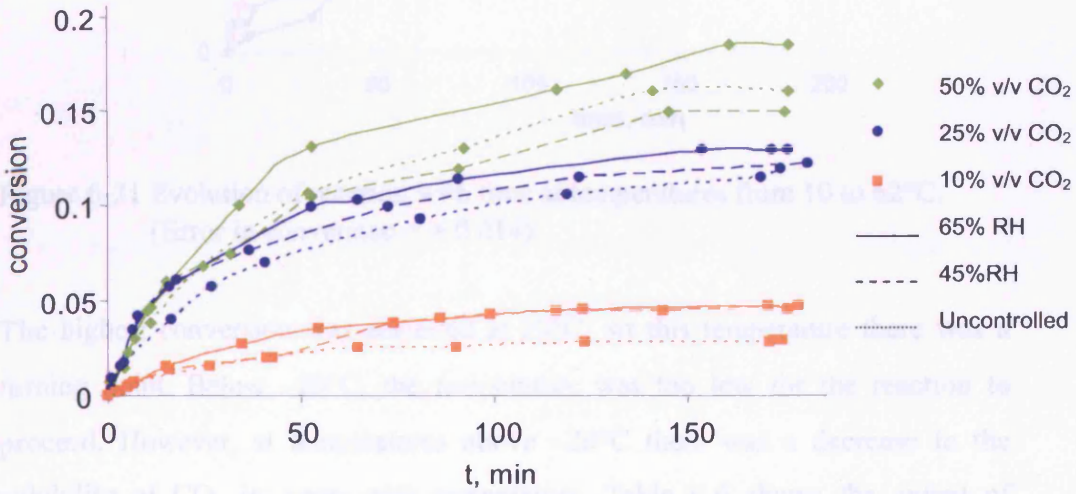

Figure 6-20 Evolution of reaction with time at CO_2 concentration from 10 to 50% at uncontrolled relative humidity and relative humidities of 45% and 65%. (Error in conversion = ± 0.014)

The results of this work (see Figure 6-20) agree with the literature, in that the optimum relative humidity for carbonation is 65% [17, 24, 48, 51].

6.3.3.4 Effect of temperature

The reaction of APCr with CO_2 was studied at temperatures of 10°C, 23°C, 43°C and 62°C. The experimental results are shown in Figure 6-21 in terms of conversion vs. time t. As expected, from these experiments it can be seen that the reaction rate increased as temperature increased.

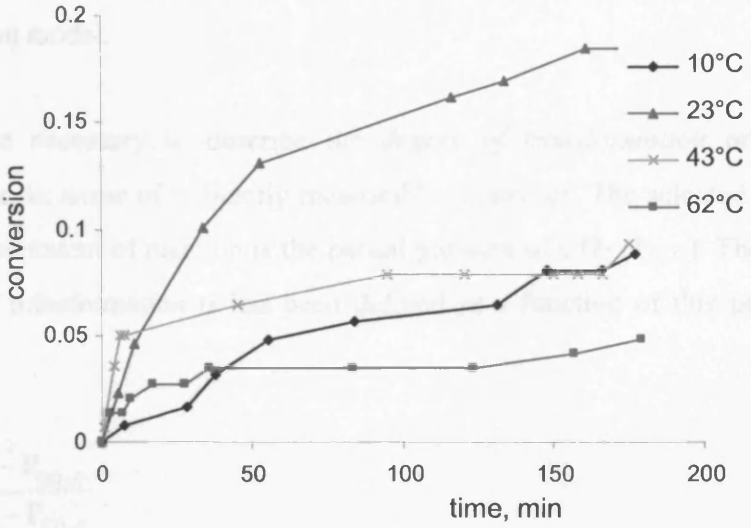

Figure 6-21 Evolution of reaction with time at temperatures from 10 to 62°C. (Error in conversion = ± 0.014)

The highest conversion was achieved at 23°C. At this temperature there was a turning point. Below ~20°C, the temperature was too low for the reaction to proceed. However, at temperatures above ~20°C there was a decrease in the solubility of CO_2 in water with temperature. Table 6-6 shows the extent of carbonation achieved at the different temperatures examined.

T, °C	% Weight gain upon carbonation ± 0.12	Conversion ± 0.014
10	9.06	0.088
23	10.09	0.185
43	12.28	0.093
62	9.88	0.048

Table 6-6 Extent of carbonation at different temperatures

6.3.3.5 Kinetic Model

Carbonation has been shown to be a diffusion controlled reaction [17, 42]. In a diffusion limited reaction, the overall rate is determined by the movement of one or more reactant species to, or a product from, a reaction interface [100]. The search for a mathematical description of the experimental data is aimed at determining the kinetic triplet: frequency factor (A), activation energy (E_A) and the reaction model.

First, it is necessary to describe the *degree of transformation* or *fractional reaction* α, in terms of a directly measurable parameter. The selected variable to monitor the extent of reaction is the partial pressure of CO_2 (P_{CO2}). Therefore, the degree of transformation α has been defined as a function of this parameter as follows:

$$\alpha = \frac{P_{CO_2} - P_{CO_2 0}}{P_{CO_2 f} - P_{CO_2 0}} \tag{6.10}$$

When calculating α, an initial induction period of 3 minutes was also taken into account, as previously explained for the conversion.

The fractional reaction α is related to the experimental data as follows [108]:

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E_A}{RT}\right) f(\alpha) \tag{4.13}$$

When the reaction is carried out at constant temperature, integration of (4.13) gives:

$$g(\alpha) = \int_0^{\alpha} \frac{d\alpha}{d\, f(\alpha)} = \int_0^{t} k(T)\, dt \tag{4.14}$$

The expressions of g(α) corresponding to the most widespread diffusion controlled mechanisms for the kind of system under study were explained in 4.6 are summarised in Table 6-7. Notice the boundary conditions of each model are limited only at the initial stage where the reacted layer is thin.

Kinetic model	**g (α)**	
Parabolic law	$\alpha = (k_A\, t)^{1/2}$	(4.15)
Logarithmic law	$\alpha = k_1 \log(k_2\, t + k_3)$	(4.16)
Linear law	$\alpha = k_1\, t + k_2$	(4.17)
Holt-Cutler-Wadsworth equation	$(1-\alpha)\ln(1-\alpha)+\alpha = \frac{k_1}{r^2}\, t$	(4.18)
Jander equation	$\left[1-(1-\alpha)^{1/3}\right]^2 = \frac{k}{r^2}\, t$	(4.19)
Ginstling-Brounshtein equation	$\left(1-\frac{2\alpha}{3}\right)-(1-\alpha)^{2/3} = \frac{k}{r^2}\, t$	(4.20)
Zhuralev-Lesokhin-Tempelman equation	$\left[(1-\alpha)^{-1/3}-1\right]^2 = \frac{k}{r^2}\, t$	(4.22)
Dunwal-Wagner equation	$\ln\left\{\frac{6}{\pi^2(1-\alpha)}\right\} = \frac{\pi^2 D}{r^2}\, t$	(4.23)
Komatsu-Uemura equation	$\left[(1+\alpha)^{1/3}-1\right]^2 = \frac{k}{r^2}\, t$	(4.24)

Table 6-7 Algebraic expressions for the kinetic models considered in this work [100, 108, 109]

To distinguish between the different models, parallel microscopic observations help to distinguish the interface geometry. X-Ray Diffraction measurements give more detailed characterisation of the phases present [108].

Figure 6-22 shows the evolution of the fractional reaction α with time at different concentrations of CO_2. The shape of α-t curves are sensitive to the relative ease of nucleation. When there is a slow development of a restricted number of nuclei, the curve has a sigmoidal shape. In the case of carbonation of MSWIr, the α-t curve in this rate process is deceleratory throughout. This is explained by the fact that there are many product particles formed rapidly at the beginning of the reaction [100] on the surfaces of the particles.

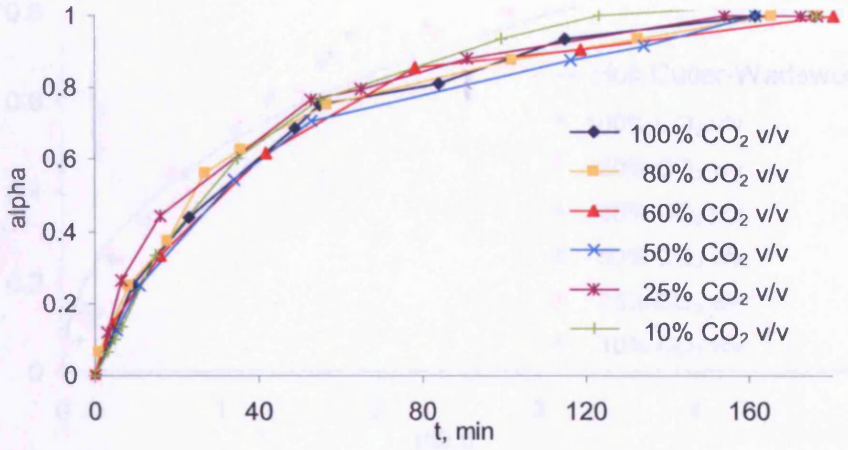

Figure 6-22 Alpha (α) - t curve for different values of CO_2 concentration. (Error in α = ± 3%)

To identify the rate equation, two different methods have been followed:

i. Comparing the shape of α-reduced time plots with lines obtained from numerical data given in literature
ii. Testing the linearity of a plot of *g* (α) against time

To compare the experimental data with the equations in Table 6-7, a reduced time scale $t/t_{0.5}$ was used, where $t_{0.5}$ corresponds to α = 0.5. For each model, single curves of α versus $t/t_{0.5}$ were obtained from numerical data given in the literature [109, 118]. Those values were directly compared to experimental data obtained for all values of temperature, water-to-solid ratio and partial pressure of CO_2, that is, variables for which the specific g(α) remained valid. As the kinetic characteristics of the system under study could change during the progress of the reaction, the scaling of the time helped to correct this effect.

The experimental data were compared to each rate equation for diffusion controlled reactions to see which gave the best fit. The model best fitting the data was the Holt-Cutler-Wadsworth model (4.18) for two-dimensional diffusion as shown in Figure 6-23. The Ginstling-Brounshtein model for three-dimensional diffusion (4.20) was the second best fitting the experimental data. The correlation for this model was just below that for Holt-Cutler-Wadsworth model.

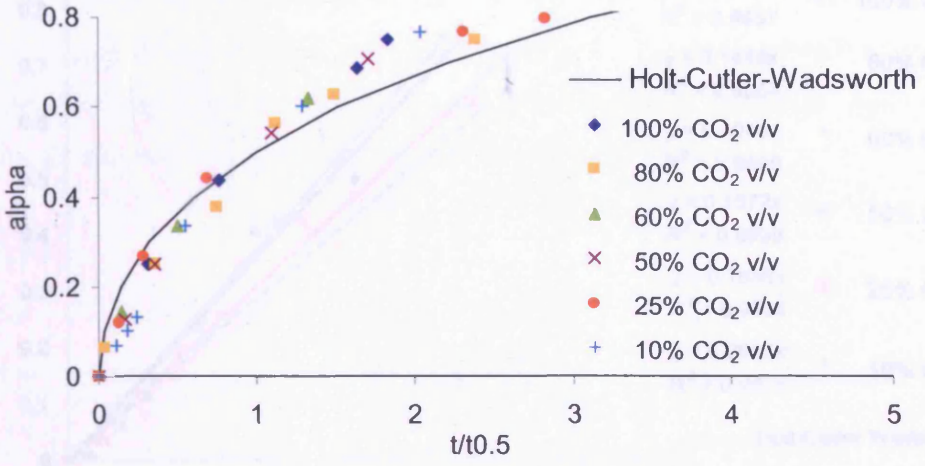

Figure 6-23 Alpha (α) vs. $t/t_{0.5}$ for concentrations of CO_2 from 10 to 100% v/v compared to the Holt-Cutler model. (Error in $\alpha = \pm 3\%$)

The Holt-Cutler-Wadsworth model fitted the experimental data with a correlation value of 0.9971. The fit is better at initial stages of the reaction and the uncertainty experienced towards the end of the reaction can be attributed to a combination of effects such as particle size variation, sintering etc. (see below). In addition, it should be noted that the algebraic form of the Holt-Cutler-Wadsworth model is inapplicable to measured data in the limit, α=1.00, which can only be reached when $t = \infty$.

The linearity of a plot of $g(\alpha)$ against time was also tested and compared to the data given in literature for the different models. The slope is the rate coefficient of the overall reaction, as shown in equation (4.27). Therefore, for isothermal experiments, the lines should have the same slope at each concentration. Figure 6-24 shows the results of this approach for concentrations of CO_2 from 10 to 100% compared to the Holt-Cutler-Wadsworth model. The correlation coefficient of each line is shown in the graph.

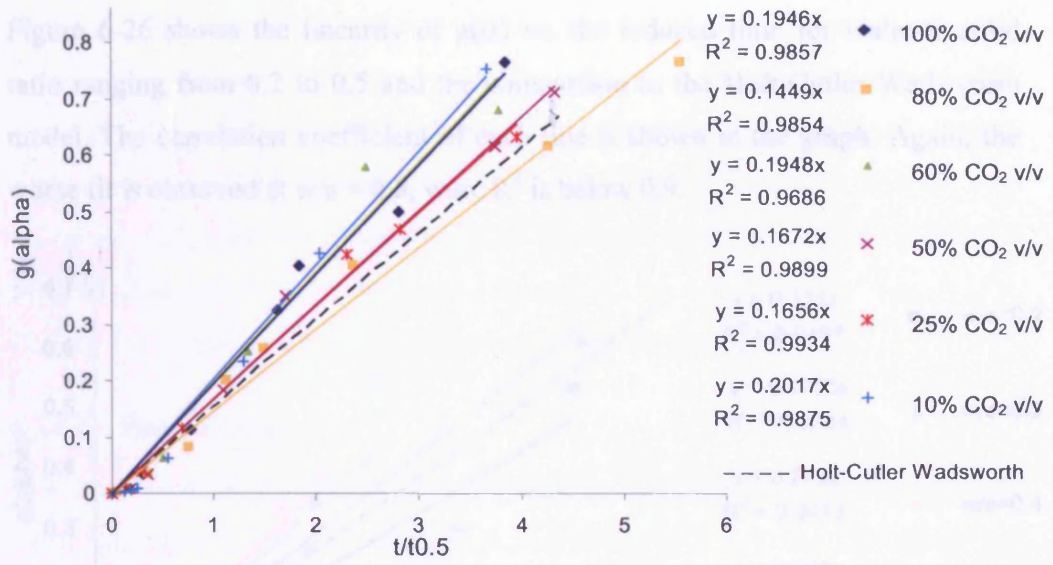

Figure 6-24 g (α), vs. $t/t_{0.5}$ for concentrations from 10 to 100% v/v CO_2 and the equations of linear regression at each CO_2 concentration. (Error in g (α) = ± 2%)

Figure 6-25 shows the fit of the Holt-Cutler-Wadsworth model to the experimental curves of α versus $t/t_{0.5}$ for different water-to-solid ratios. The graph shows that the selected model fits the experimental values well. However, the fit is poorest for w/s = 0.5 and if this data is disregarded, the correlation value is 0.99.

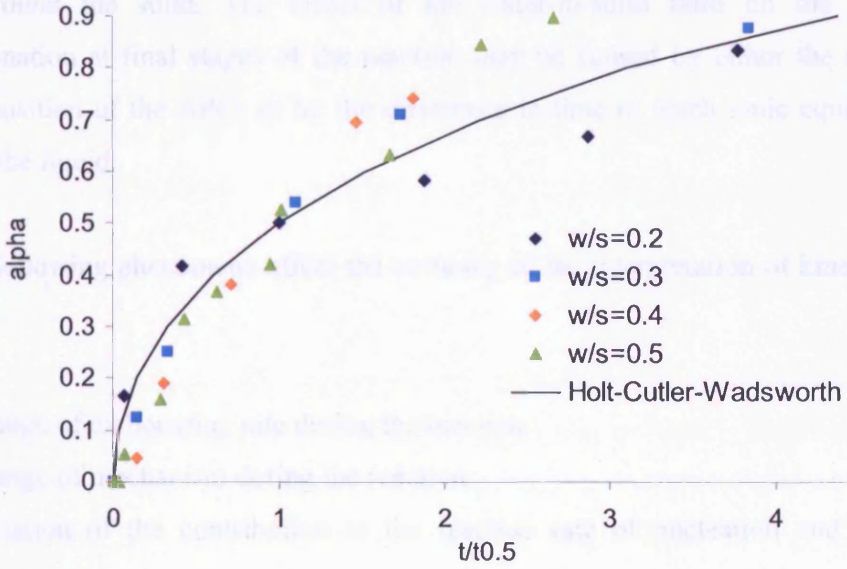

Figure 6-25 Alpha (α) vs. $t/t_{0.5}$ for water-to-solid ratio from 0.2 to 0.5 compared to the Holt-Cutler-Wadsworth model. (Error in α = ± 3%)

Figure 6-26 shows the linearity of g(α) vs. the reduced time for water-to-solid ratio ranging from 0.2 to 0.5 and the comparison to the Holt-Cutler-Wadsworth model. The correlation coefficient of each line is shown in the graph. Again, the worse fit is observed at w/s = 0.5, were R^2 is below 0.9.

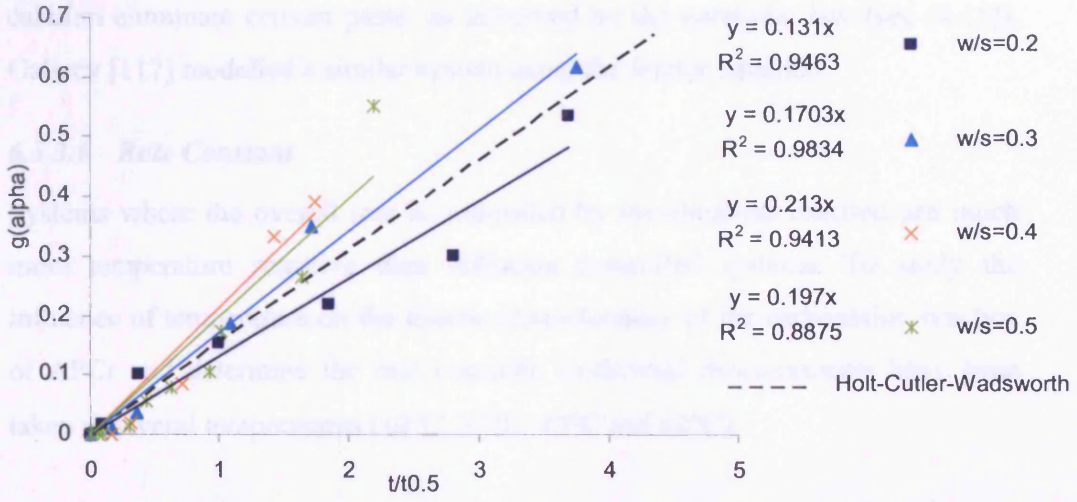

Figure 6-26 g (α), vs. $t/t_{0.5}$ for water-to-solid ratio from 0.2 to 0.5 and the equations of linear regression at each w/s ratio. (Error in g (α) = ± 2%)

The difference experienced at w/s = 0.5 can be attributed to the excess of water in or around the solid. The effect of the water-to-solid ratio on the rate of carbonation at final stages of the reaction may be caused by either the residual composition of the APCr or by the difference in time to reach ionic equilibrium with the liquid.

The following phenomena affect the accuracy of the interpretation of kinetic data [100]:

- change of carbonation rate during the reaction
- change of mechanism during the reaction
- variation of the contribution to the reaction rate of nucleation and growth processes
- influence of organics or heavy metal complexes

Systems of similar nature to MSWIr have been found to carbonate following a similar diffusion-limited kinetic model [112]. For example, Nishikawa et al. [92] found that the carbonation of synthesised ettringite ($3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}32H_2O$) could be modelled by the Jander equation (see (4.19)), whilst Goñi et al. [49] described the accelerated carbonation of Friedel's salt ($Ca_4Al_2O_6Cl_2{\cdot}10H_2O$) in calcium aluminate cement paste, as governed by the parabolic law (see (4.15)). Galwey [117] modelled a similar system using the Jander equation.

6.3.3.6 Rate Constant

Systems where the overall rate is controlled by the chemical reaction are much more temperature sensitive than diffusion controlled systems. To study the influence of temperature on the kinetic characteristics of the carbonation reaction of APCr and determine the rate constant, isothermal measurements have been taken at several temperatures (10°C, 23°C, 43°C and 62°C).

As shown in equation (4.26), reaction rates are related to α and to temperature, T, by different and independent functions. A complete kinetic description of behaviour requires characterisation of both expressions:

$$\frac{d\alpha}{dt} \propto f(\alpha)k(T) \qquad (4.26)$$

The best way of measuring the influence of temperature on reaction rate is to separate variables by first determining isothermal curves at different temperatures and expressing each set of observations as $g(\alpha)$ vs. t, according to equation (4.27):

$$g(\alpha) = k\,t \qquad (4.27)$$

The experimental data have been collected in a single plot for comparison, see Figure 6-27. The change in kinetic behaviour can be easily appreciated. As expected, the speed of reaction was higher at higher temperatures. In the figure the equations of the linear fit of the experimental data to equation (4.27) are also shown with their corresponding correlation coefficient R^2. The slope of each line equals the experimental value of the rate constants at each temperature. The obtained values are summarised in Table 6-8.

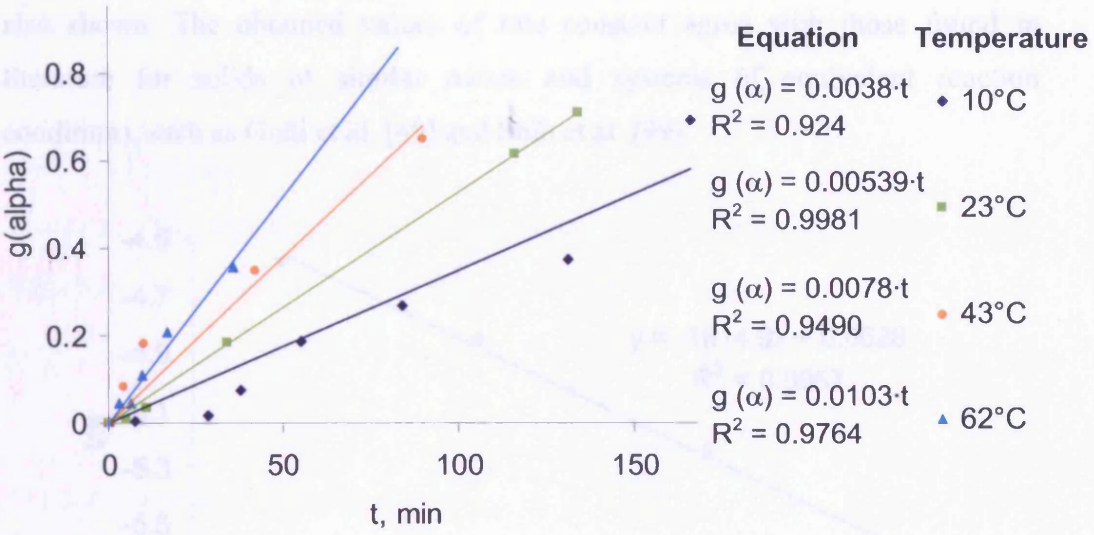

Figure 6-27 g (α), vs. $t/t_{0.5}$ for temperatures from 10 to 62°C and the equations for the linear regression at each temperature. (Error in g (α) = ± 2%)

T, °C	10	23	43	62
k, min^{-1}	0.0038	0.00539	0.0078	0.0103
error k, min^{-1}	± 0.0003	± 0.00016	± 0.0004	± 0.0005

Table 6-8 Experimental values of rate of reaction (k), at each temperature.

As explained in section 4.7, the relationship between k and T has been assumed to obey the Arrhenius equation:

$$k = A \exp\left(-\frac{E_A}{RT}\right) \qquad (4.28)$$

However, for solid reactions it is not always considered particularly reliable (see section 4.7.1) [111, 119, 120]. This approach is the most widely accepted and, independently of the physical meaning of A and E_A, is a well-established method of comparing kinetic data. As previously explained, in solid reactions there is little known about alternative relationships to the Arrhenius equation, but some studies have shown that this model is not necessarily the only or the best expression for all reactions [100].

The experimental values of k at different temperatures (see Table 6-8) have been fitted to equation (4.28). Figure 6-28 shows the Arrhenius plot for the experimental data of ln(k) vs. 1/T. The equation and correlation coefficient are

also shown. The obtained values of rate constant agree with those found in literature for solids of similar nature and systems of equivalent reaction conditions, such as Goñi et al. [49] and Shih et al. [99].

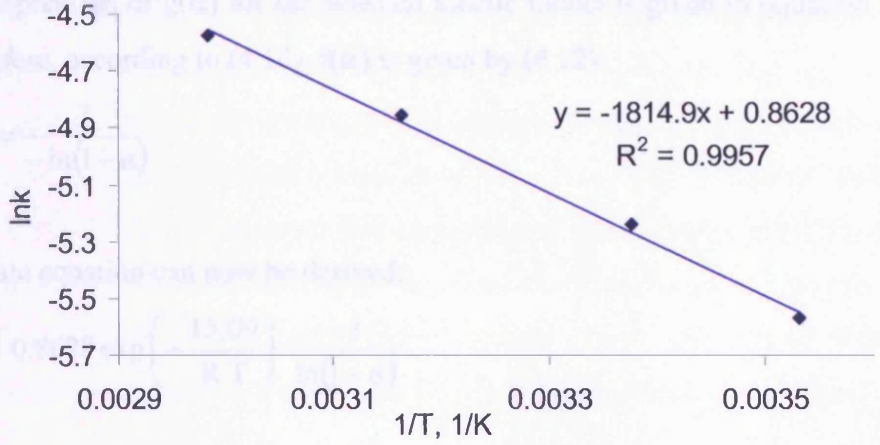

Figure 6-28 Arrhenius plot for the experimental data

Thus, the following expression for the rate constant can be derived:

$$k = 0.8628 \exp\left(-\frac{15.09}{RT}\right), \text{min}^{-1} \qquad (6.11)$$

The low value of E_A (15.09 kJ/mol) is within the range of values for diffusion control and it is lower that the usual values for chemical reaction control [97]. At low temperatures, bulk diffusion in a polycrystalline material is dominated by surface diffusion along the grain boundaries because volume diffusion through the structure is too slow [112]. This process has a lower E_A. As temperature increases, volume diffusion, with a higher E_A, becomes the dominant diffusion mechanism.

As mentioned above, the meaning of the Arrhenius parameters when dealing with reactions in the solid state is subject to debate. Given that k has contributions from nucleation and growth processes, the determination of the Arrhenius parameters is influenced by the selection of the kinetic model. This is one of the main disadvantages of using Arrhenius to determine the rate constant. In general, the meaning of E_A has to be treated cautiously. It is a measure of the temperature dependence of the rate of reaction carried out under a certain set of experimental conditions. Before extrapolating this value to a different set of conditions, it is

necessary to demonstrate that the mechanism is still the same as that operating during the experiment [112, 115].

6.3.3.7 Rate Equation

The expression of g(α) for the selected kinetic model is given in equation (4.18). Therefore, according to (4.14), f(α) is given by (6.12):

$$f(\alpha) = \frac{1}{-\ln(1-\alpha)} \tag{6.12}$$

The rate equation can now be derived:

$$\frac{d\alpha}{dt} = 0.8628 \exp\left(-\frac{15.09}{RT}\right) \cdot \frac{-1}{\ln(1-\alpha)} \tag{6.13}$$

Equation (6.13) describes the progress of the carbonation reaction of APCr in a batch system at a pressure of 3 bars and relative humidity of 65%. It is valid for concentrations of CO_2 in the range of 10-100% and at w/s ratios from 0.2 to 0.4.

It is important to specify the experimental conditions in which the reaction was carried out, as many studies have shown that the same process cannot be characterised by the same kinetic triplet under different experimental conditions [121].

6.3.3.8 Reaction mechanism

Reactions in the solid state, such as carbonation, usually have a multi-step nature, which would imply the combination of two or more kinetic models. Therefore, depending on the considered reaction performed at different temperatures, the choice of the kinetic models influences the determination of the reaction mechanism [107].

The results obtained in the kinetic analysis suggest that the following carbonation mechanism for APCr can be considered. When the APCr contact with water, which contains carbonate ion and has a low pH, the solid and the liquid phases are not in equilibrium. At first, alkali chlorides, together with some calcium, magnesium, zinc, lead and cadmium salts rapidly dissolve into the liquid from the

surface of the particles [81]. The carbonation reaction proceeds in a diffusion controlled fashion through the surface of the solid. Thus, the calcium ions in the liquid are consumed to form $CaCO_3$.

The reactions (6.4) to (6.9) shown earlier describe the process above. These reactions are very fast in bulk aqueous solution. However, the rate of these reactions may be reduced for a very thin adsorbed water film [99]. Reaction (6.5) represents the adsorption and hydration of CO_2. These two processes can happen at the surface in the water layer that covers both $Ca(OH)_2$ and $CaCO_3$. Given that the reaction is diffusion controlled, these are the slowest steps. The rate of the dissolution of $Ca(OH)_2$ is faster, since the ash is thoroughly mixed with water prior to carbonation, thus the Ca^{2+} and OH^- ions should already be present.

As carbonation progresses, the product particles precipitate on the surface of the ash particles and build up a thicker product layer that increases the resistance to the penetration of CO_2. Therefore the diffusion through the product layer will become more significant at the final stages of reaction. In the present work, carbonation was observed to virtually cease after 3 hours. However, it may well continue over longer periods, but at a very slow rate.

6.3.3.9 Analytical support

Mineralogical changes

As previously mentioned, X-Ray Diffraction measurements provide a more detailed characterisation of the mineral phases present. Figure 6-29 shows the X-Ray diffractograms of APCr from the SELCHP incinerator before and after carbonation at the optimum conditions.

Aragonite is the preferred form of $CaCO_3$ generated in the presence of chloride [49]. However, the diffractogram shows that despite the high concentration of chloride in the form of NaCl and KCl in APCr, calcite was formed in preference to aragonite. The presence of vaterite was also observed, which is known to be formed through a direct reaction of the carbonate ion in the presence of water

vapour with the calcium ion in the solid [92]. Calcite is the most stable form of $CaCO_3$ at ambient temperature.

It is worth noting the absence of $Ca(OH)_2$ after carbonation, as well as the lower intensity of the peaks of $CaSO_4$, NaCl and $CaCl_2$ due to the dissolution and reaction of the alkaline salts.

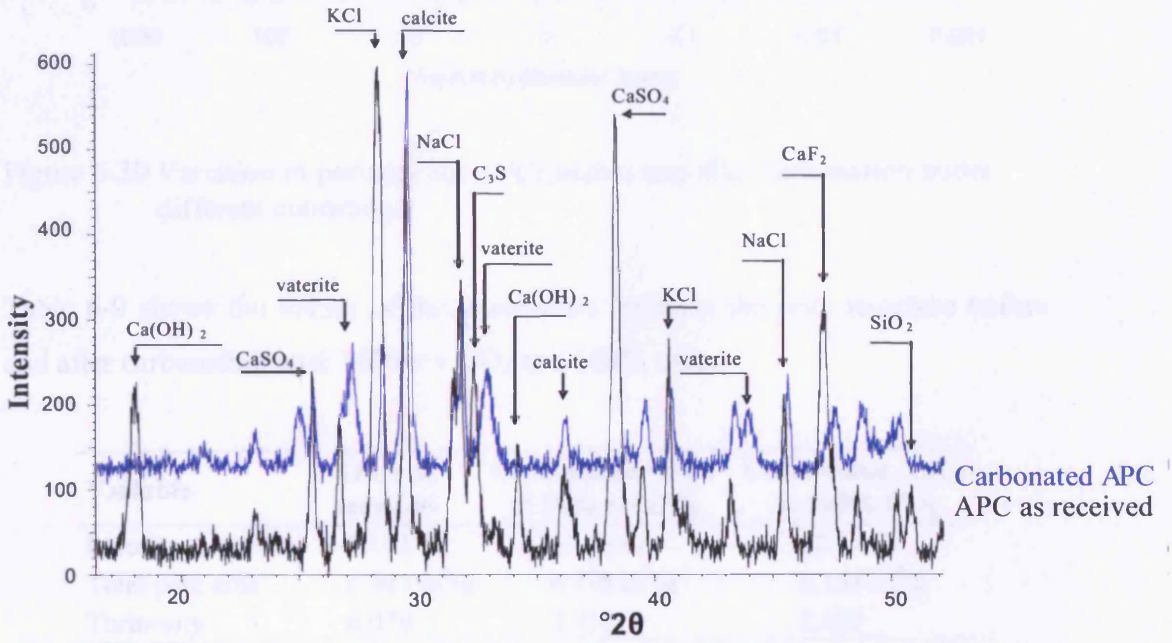

Figure 6-29 XRD Diffractograms of APCr from SELCHP incinerator before and after carbonation

Pore structure changes

Figure 6-30 shows how the pore structure changes before and after carbonation. The reduction in porosity results from a larger molar volume of calcite relative to the initial $Ca(OH)_2$ and from carbonation-related shrinkage. In addition, the $CaCO_3$ formed has a very low solubility and will therefore contribute to the blocking of the pore system.

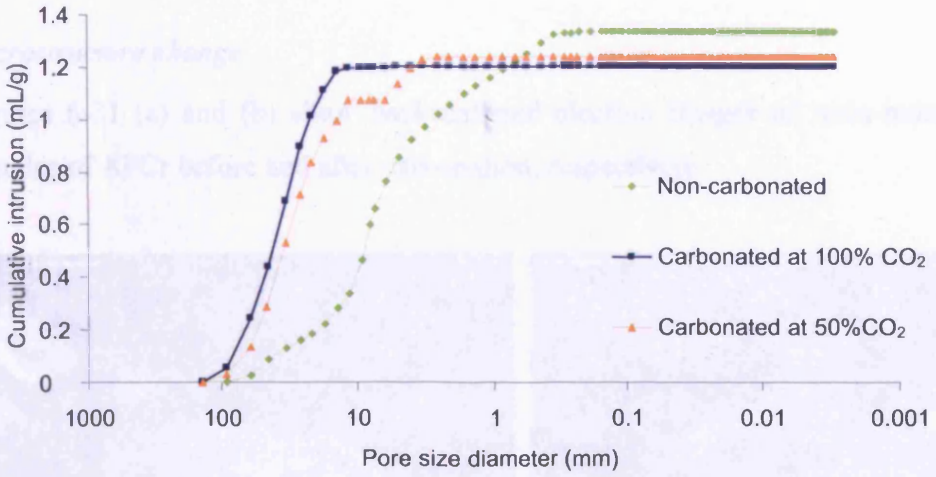

Figure 6-30 Variation in porosity for APCr before and after carbonation under different conditions.

Table 6-9 shows the values of the parameters defining the pore structure before and after carbonation with 50% v/v CO_2 and 100% CO_2.

Variable	APCr as received	Carbonated APCr at 50% v/v CO_2	Carbonated APCr at 100% CO_2
Porosity	73.05 %	67.46 %	62.37 %
Total pore area	4.387 m^2/g	0.298 m^2/g	0.143 m^2/g
Tortuosity	6.079	2.918	2.687

Table 6-9 Pore structure values for SELCHP APCr before and after carbonation

The reduced porosity makes diffusion much slower than in non-carbonated ash. The decreased tortuosity showed the absence of microcracking or pore redistribution effects, which are typical effects when wastes of similar nature are treated by stabilisation/solidification techniques [42, 51]. The reduction in the value of the total pore area is also rather significant.

The evolution of the pore structure supports the description of the carbonation mechanism given in section 6.3.3.8. As carbonation progresses, the product particles precipitate on the surfaces of the ash particles. Given the microporous nature of the APCr, the small pores are blocked rapidly by the product and the surfaces are no longer available for the reaction to take place.

Microstructure change

Figures 6-31 (a) and (b) show backscattered electron images of resin-mounted samples of APCr before and after carbonation, respectively.

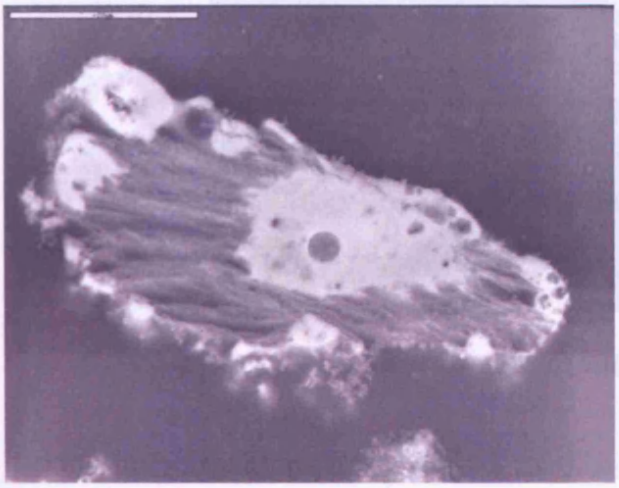

Figure 6-31 (a) BSI of resin mounted APCr before carbonation

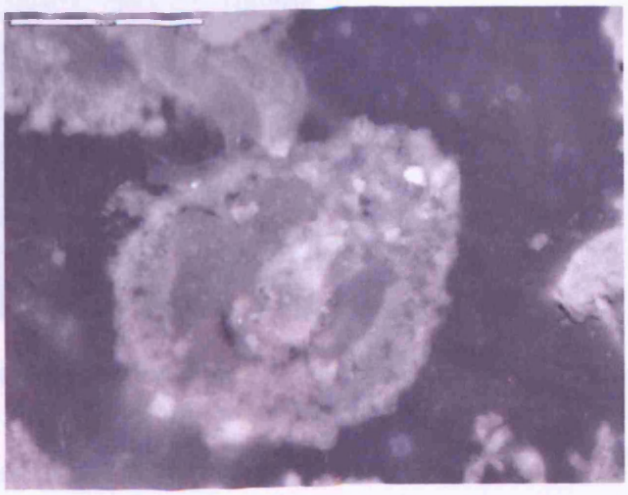

Figure 6-31 (b) BSI of resin mounted APCr after carbonation

The size of the two particles was similar and the measurement of the cross-sectional areas gave values of 1096.8 μm^2 and 1039.6 μm^2 for (a) and (b), respectively. In the images, an increase of the thickness of the outer ring of the particle can be easily appreciated from 2.41μm to 6.75μm.

Analysis of the sample surfaces by EDAX showed that the light grey area was a calcium deficient region, whilst the dark grey coloured zone was carbonate infilling the porous region. In the centre of the particle (b), there was an un-reacted core of material. This supports the assumption that carbonation follows the unreacted core model, in addition to the results obtained in the experimental determination of the controlling mechanism.

Figure 6-32 shows the APCr after carbonation where the reaction product can easily be appreciated as a precipitate on the surface of the ash particles.

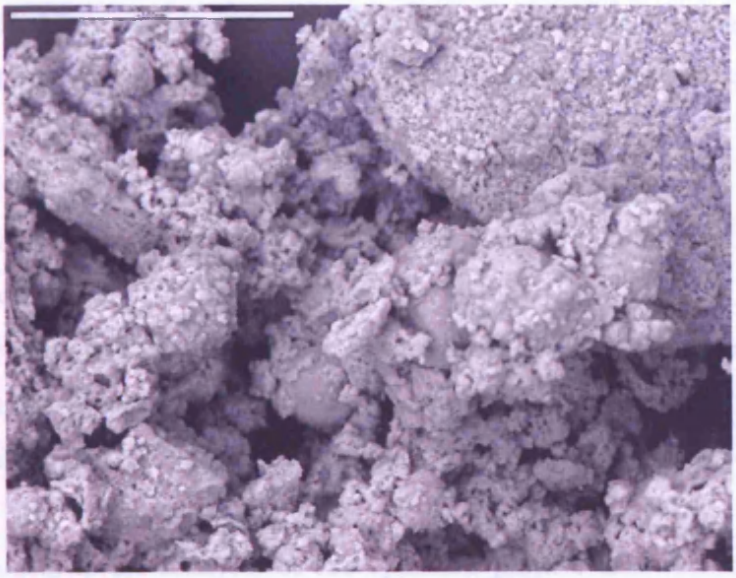

Figure 6-32 APCr after carbonation

SEM observation of the carbonated samples showed that there was little variation on the basic shape of the ash particles, but their surfaces were rougher and were shown to be covered with carbonate reaction products. The reaction is initiated on all surfaces, which is consistent with the reaction model proposed of a growing barrier layer of product between the CO_2 and the solid.

During the reaction, the initially loose particles of the reactant powder stick together and become aggregated. This is further evidence of the mobility of surface participating species and the formation of interparticulate material.

6.4 Influence of Particle Size on Reaction Kinetics

The reaction of APCr with CO_2 requires consideration of the specific characteristics of heterogeneous rate processes such as particle sizes and shapes, compositional and structural factors in addition to the reactant pressure and temperature. Some authors even recognise that there may be irreproducibility of observations between experiments with different preparations of (apparently) the same solid reactant [117].

In this section the influence of the size factor in the evolution of the carbonation reaction is studied. The particle size distribution of APCr from the SELCHP incinerator is not as wide as the particle size distribution found in other APCr (see

section 5.4.1), however it is wide enough to play a role in influencing the kinetics of carbonation. Three size fractions were separated, as described in section 5.5.2.3:

- 0 μm <d < 45 μm
- 45 μm < d < 90 μm
- 90 μm < d

Parallel experiments were carried out with unclassified APCr. Previous results of carbonation of unclassified ash were not used for comparison due to the carbonation that the APCr may have undergone during storage.

This study follows the analysis of the optimum particle size showed in section 6.2.2. The selected limiting size for carbonation was found to be below 212 μm for APCr. As previously mentioned, 95 % of the SELCHP APCr was below that size therefore, the unclassified fraction falls within the limiting particle size. However, for any other APCr "unclassified" means "no further classified below 212 μm".

6.4.1 Carbonation at Different Particle Sizes

The conditions used for carbonation were the same ones as above: 65% relative humidity, pressure of 3 bars and carbonation time of 3 hours. APCr was exposed to concentrations of CO_2 ranging from 25 to 100% and the water-to-solid ratio was varied from 0.2 to 0.5.

6.4.1.1 Extent of Carbonation

The conversions and the weight gain upon carbonation for the three size fractions and the unclassified ash at the optimum conditions for carbonation and 50% v/v CO_2, are shown in Table 6-10.

Particle size fraction	% Weight gain upon carbonation ± 0.12	Conversion ± 0.014
0 μm <d < 45 μm	11.70	0.174
45 μm < d < 90 μm	11.79	0.123
90 μm < d	9.67	0.129
Unclassified	12.53	0.191

Table 6-10 Effects of particle size on the carbonation of APCr

As indicated in the table, the d > 90 μm fraction was the least reacted whilst the 0 μm < d < 45 μm has the highest conversion of the three classified fractions. This could be due to the higher surface area of the smaller fraction. As previously mentioned, the presented surface of the APCr has an important influence on the reaction with CO_2. The unclassified fraction was the most reacted. This could be partly due to partial natural carbonation of the APCr during the sieving process.

When comparing the weight gain upon carbonation for the three size fractions, the d > 90 μm fraction showed the lowest weight gain of the three, whilst the unclassified fraction shows again the highest extent of carbonation 12.53%, in line with the conversion results.

In a powder having the characteristics of APCr, the larger the size range and the narrower the particle size distribution, the higher is the voidage. When there is a substantial mixture of different particle sizes there are more surfaces made available for the CO_2 and therefore that reaction is better which explains the higher extent of carbonation of the unclassified fraction. However, this difference in reactivity could also be due to a compositional variation between the size fractions. This possibility is considered below (see section 6.4.1.2).

The effect of particle size on the rate of carbonation reaction can be seen in Figure 6-33 in terms of conversion vs. time t. The reaction for all the samples slows down after 150min. The rate of reaction was higher for unclassified ash, followed by 0 μm < d < 45 μm. The slowest reaction rate is shown by the 45 μm < d < 90 μm fraction. Thus, the particle size of APCr influences the final conversion reached.

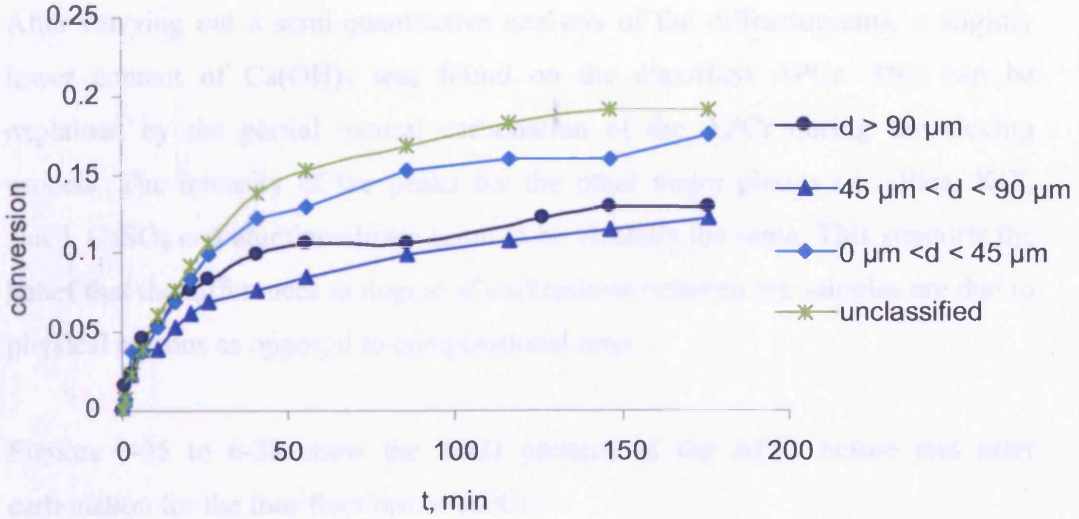

Figure 6-33 Evolution of reaction with time for the four fractions at optimum conditions. (Error in conversion = ± 0.014%)

6.4.1.2 Mineralogical Differences

One possible explanation of the variation in the degree of carbonation between the different fractions could be a variation in composition/mineral phases between the fractions, as seen in similar systems [46]. In order to test this option, XRD of every fraction was carried out before and after carbonation. Figure 6-34 shows the comparison of the X-Ray diffractograms for the four samples.

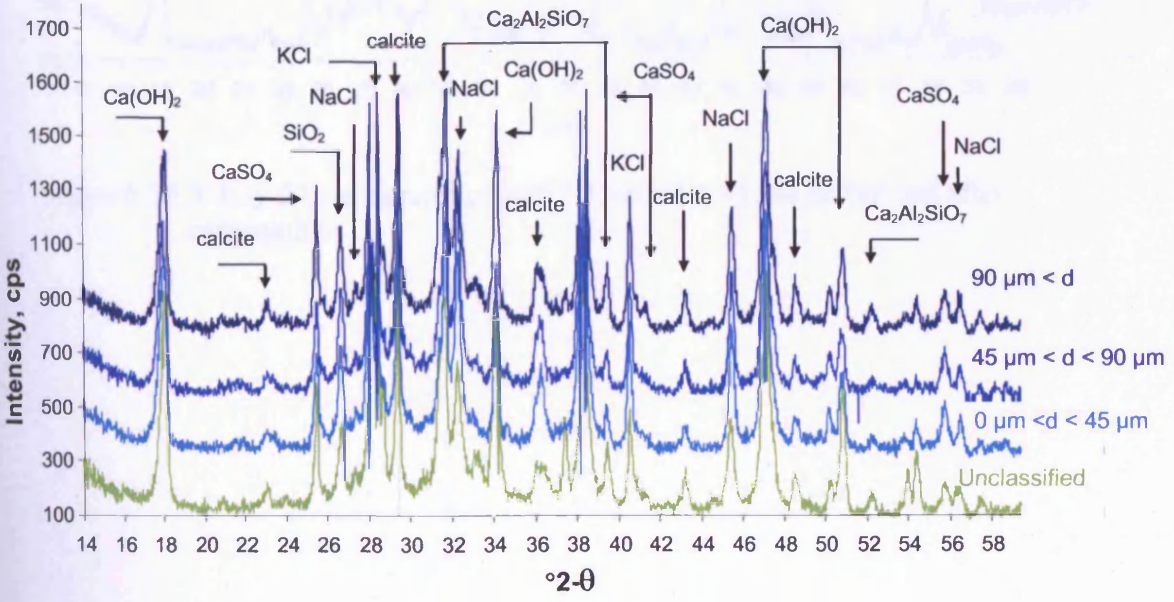

Figure 6-34 X-Ray diffractograms of APCr from SELCHP incinerator for the four size fractions before carbonation.

After carrying out a semi-quantitative analysis of the diffractograms, a slightly lower content of $Ca(OH)_2$ was found on the classified APCr. This can be explained by the partial natural carbonation of the APCr during the sieving process. The intensity of the peaks for the other major phases i.e. silica, KCl, NaCl, $CaSO_4$ and aluminosilicate seem to be virtually the same. This supports the belief that the differences in degree of carbonation between the samples are due to physical reasons as opposed to compositional ones.

Figures 6-35 to 6-38 show the XRD patterns of the APCr before and after carbonation for the four fractions of APCr.

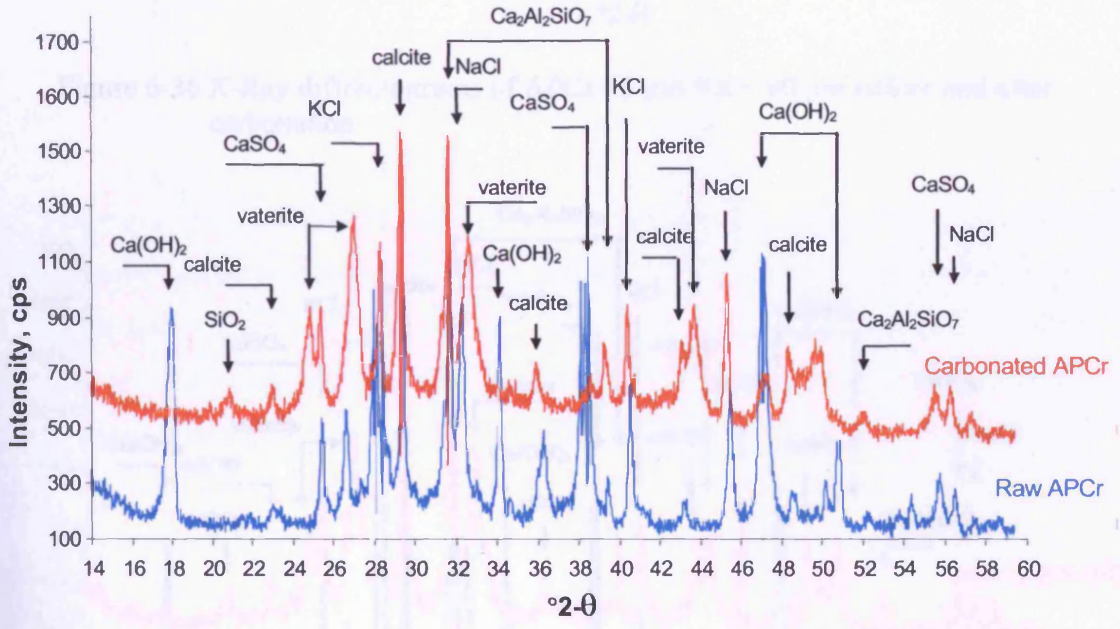

Figure 6-35 X-Ray diffractograms of APCr 0 µm <d < 45 µm before and after carbonation

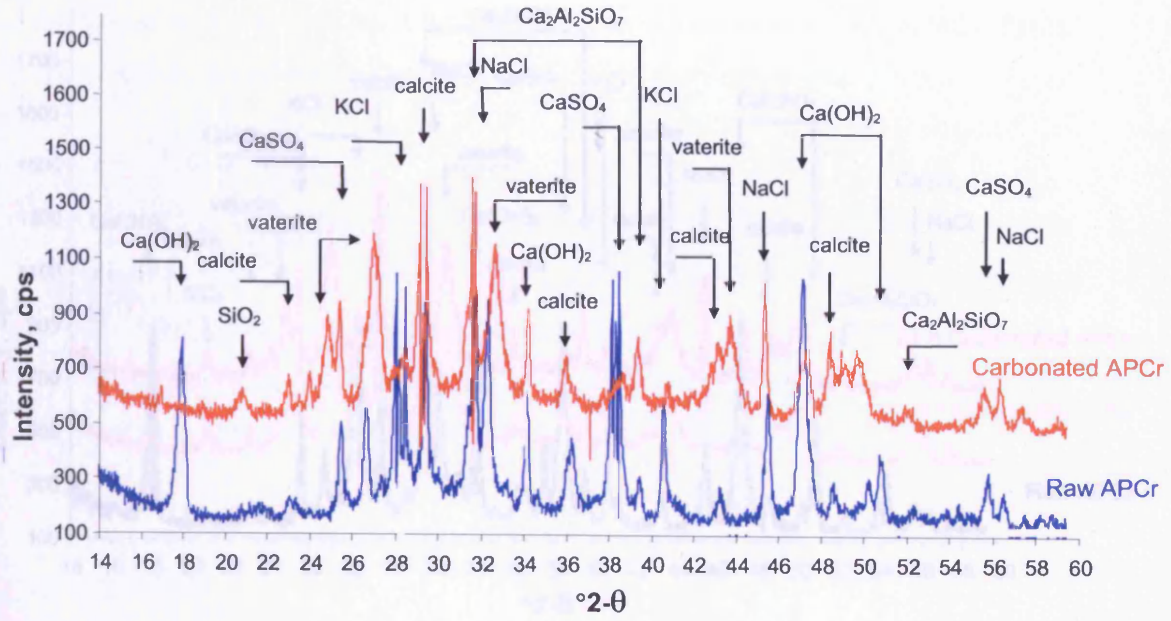

Figure 6-36 X-Ray diffractograms of APCr 45 µm < d < 90 µm before and after carbonation

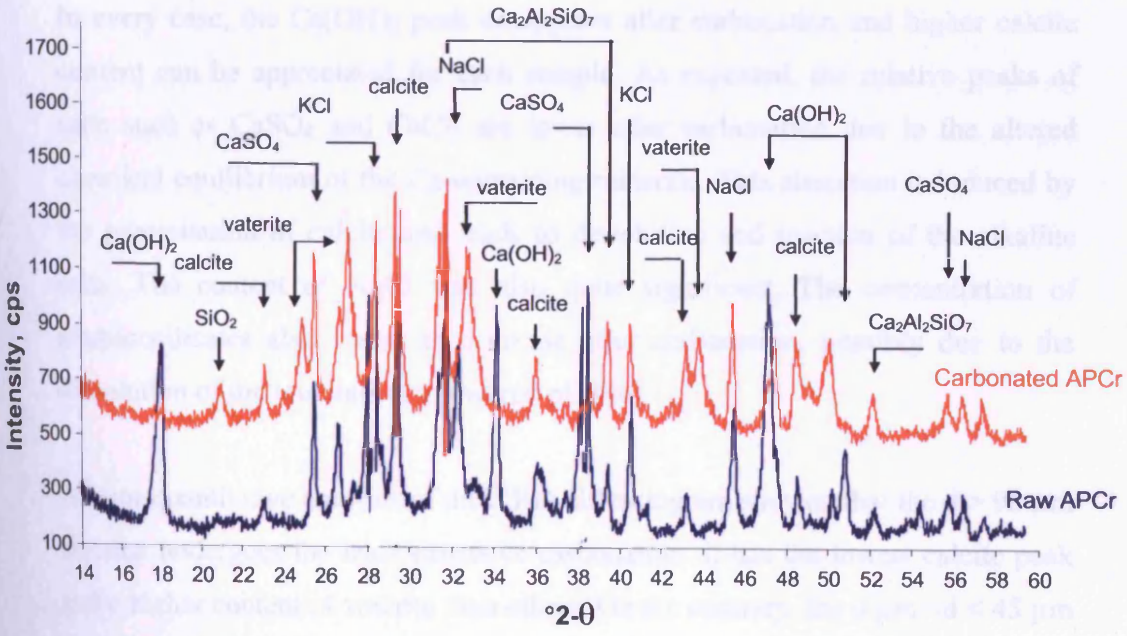

Figure 6-37 X-Ray diffractograms of APCr 90 µm < d before and after carbonation

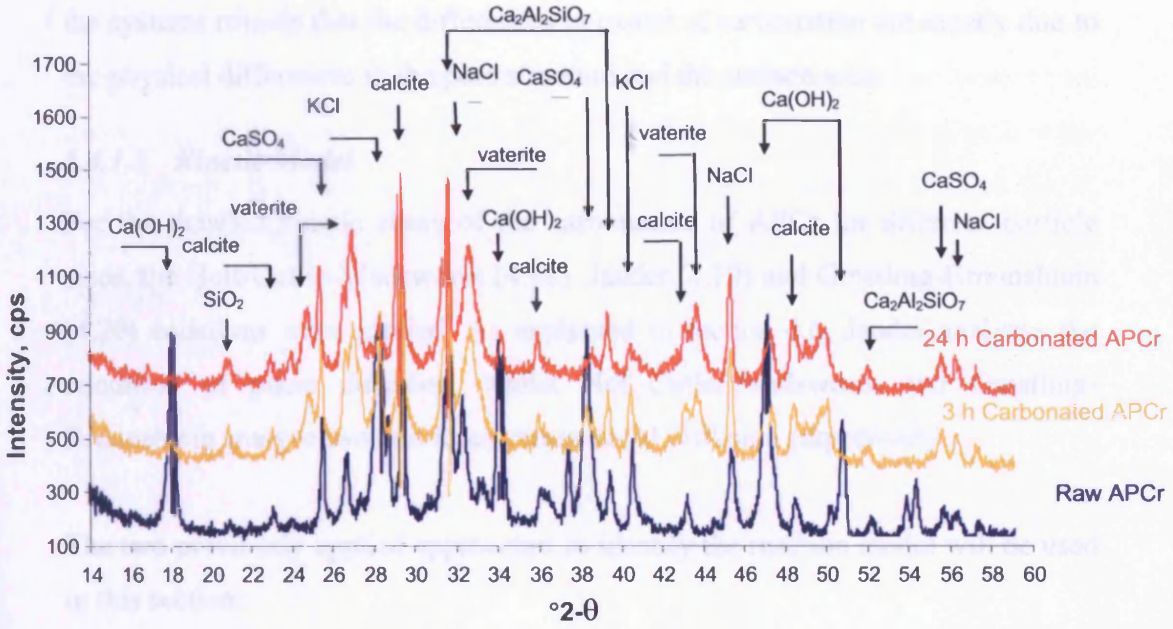

Figure 6-38 X-Ray diffractograms of unclassified APCr before carbonation and after 3 hours and 24 hours of carbonation

In every case, the $Ca(OH)_2$ peak disappears after carbonation and higher calcite content can be appreciated for each sample. As expected, the relative peaks of salts such as $CaSO_4$ and $CaCl_2$ are lower after carbonation due to the altered chemical equilibrium of the Ca-containing minerals. This alteration is induced by the precipitation of calcite and leads to dissolution and reaction of the alkaline salts. The content of NaCl was also quite significant. The concentration of aluminosilicates also seems to decrease after carbonation, possibly due to the dissolution of the minerals at a lowered pH [46].

A semi-quantitative analysis of the XRD diffractogram showed that the $d > 90$ µm fraction undergoes the least extensive carbonation. It has the lowest calcite peak and a higher content of vaterite than others. On the contrary, the 0 µm $< d < 45$ µm fraction is the most extensively carbonated of the classified fractions, followed by the 45 µm $< d < 90$ µm one. For 0 µm $< d < 45$ µm, the diffractogram shows the lowest content of $Ca(OH)_2$ after carbonation.

In line with the results shown in 6.4.1.1, the unclassified fraction was better carbonated than any of the classified ones. The mineralogy analysis showed that the unclassified fraction was fresher. However, the degree of similarity between

the systems reveals that the differences in extent of carbonation are mostly due to the physical differences in the pore structure and the surface area.

6.4.1.3 Kinetic Model

For the detailed kinetic study of the carbonation of APCr for different particle sizes, the Holt-Cutler-Wadsworth (4.18), Jander (4.19) and Ginstling-Brounshtein (4.20) equations were applied. As explained in section 4.6, Jander analyzes the condition of plane diffusion, whilst Holt-Cutler-Wadsworth and Ginstling-Brounshtein analyze two and three-dimensional diffusion respectively.

The two previously applied approaches to identify the reaction model will be used in this section:

i. Comparing the shape of α-reduced time plots with lines obtained from numerical data given in literature
ii. Testing the linearity of a plot of $g(\alpha)$ against time

Considering the value of the correlations, the Ginstling-Brounshtein model for three-dimensional diffusion (4.20) gave the best fit for the three classified size fractions, as shown in Figure 6-39. The average correlation for the three fractions was 0.99. This means that the kinetic behaviour is controlled by interface advance into an equidimensional particle subject to control by a diffusing process across a systematically increasing thickness of barrier product layer [117].

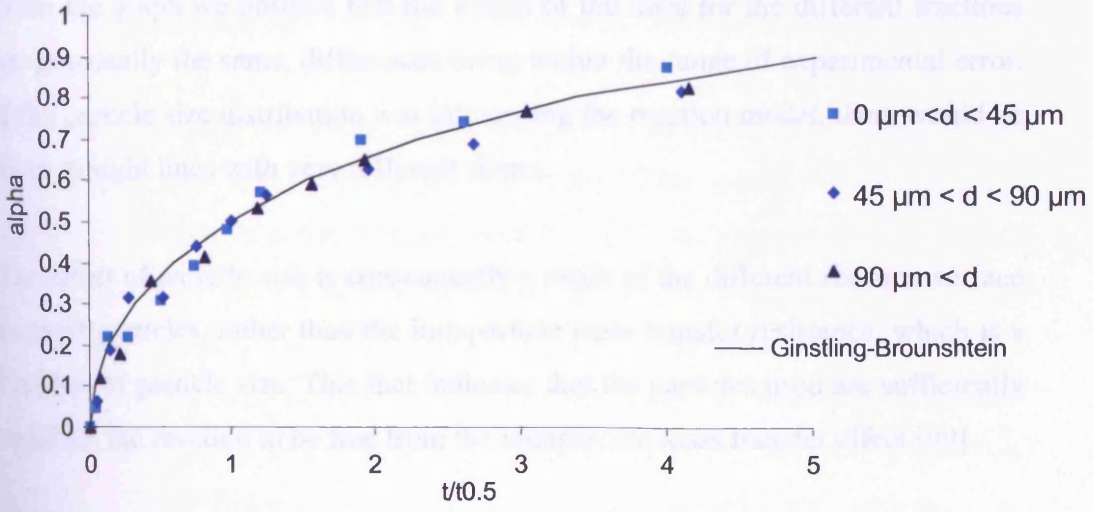

Figure 6-39 Alpha (α) vs. $t/t_{0.5}$ for concentrations from 10 to 100% v/v CO_2 compared to the Ginstling-Brounshtein model for the classified APCr. (Error in α = ± 3%)

In addition, the linearity of a plot of g(α) against time was also tested and compared to the data given in literature for the different models. The linear plot gives three straight lines passing through the origin. The slope of these lines is the rate constant, which is a variable characteristic of the reaction system alone. Therefore, for isothermal experiments, the lines should have the same slope at each concentration. Figure 6-40 shows the results of this approach for the three size fractions. The correlation coefficient of each line is shown in the graph.

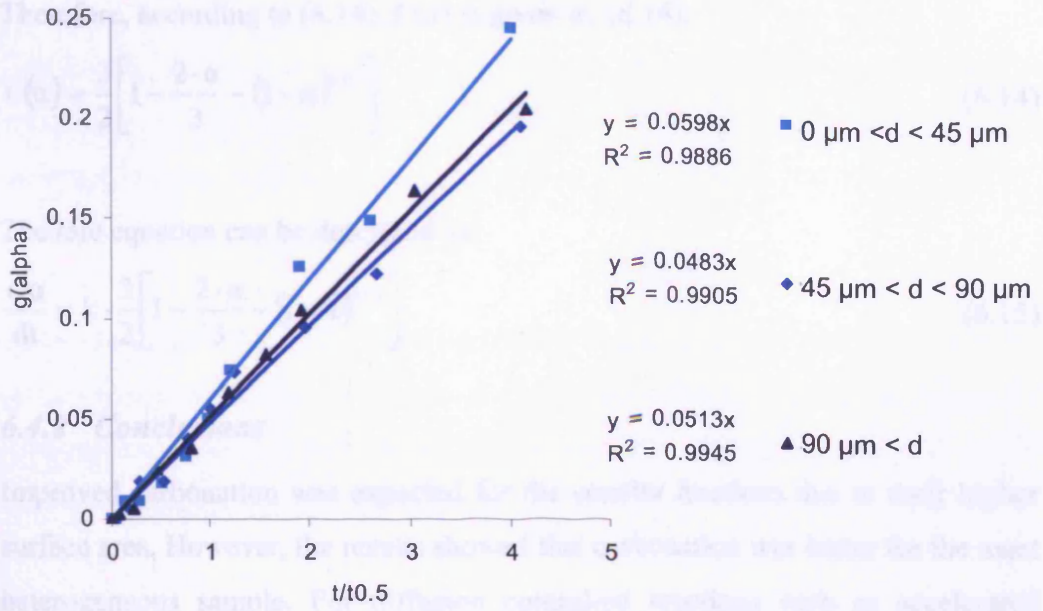

Figure 6-40 g (α) vs. $t/t_{0.5}$ for w/s from 0.2 to 0.5 compared to the Ginstling-Brounshtein model for the classified APCr. (Error in g (α) = ± 2%)

From the graph we observe that the slopes of the lines for the different fractions are practically the same, differences being within the range of experimental error. If the particle size distribution was influencing the reaction model, there would be three straight lines with very different slopes.

The effect of particle size is consequently a result of the different reaction surface areas of particles, rather than the intraparticle mass transfer resistance, which is a function of particle size. This fact indicates that the particles used are sufficiently small for the reaction to be free from the intraparticle mass transfer effect [99].

Therefore, the result of the kinetic analysis identified that the Ginstling-Brounshtein model provided the most satisfactory representation of the classified APCr. The expression of g(α) for the selected kinetic model is shown in equation (4.20):

$$\left(1-\frac{2\alpha}{3}\right)-(1-\alpha)^{2/3}=\frac{k}{r^2}t \qquad (4.20)$$

Therefore, according to (4.14), f (α) is given by (6.14):

$$f(\alpha)=\frac{3}{2}\left[1-\frac{2\cdot\alpha}{3}-(1-\alpha)^{2/3}\right] \qquad (6.14)$$

The rate equation can be described as:

$$\frac{d\alpha}{dt}=k\cdot\frac{3}{2}\left[1-\frac{2\cdot\alpha}{3}-(1-\alpha)^{2/3}\right] \qquad (6.15)$$

6.4.2 Conclusions

Improved carbonation was expected for the smaller fractions due to their higher surface area. However, the results showed that carbonation was better for the most heterogeneous sample. For diffusion controlled reactions such as accelerated carbonation, the influence of the reaction surface area of particles is fundamental. The higher extent of carbonation of the unclassified fraction has demonstrated this influence. The unclassified fraction has a larger size range and consequently, a higher voidage which results in more surfaces of the APCr presented to the CO_2.

When carbonating more homogeneous fractions of APCr, the carbonation is best modelled by the Ginstling-Brounshtein equation. This model corresponds to a diffusion controlled reaction in a sphere of radius r which agrees with the greater homogeneity of the classified solid. These are encouraging results when considering carrying out carbonation at large scale as carbonation is favoured when the ash is treated as received. There would be then no need for an additional unit operation therefore saving costs, time and energy. In addition, if the less reactive APCr fractions were separated, they would still represent an environmental burden.

6.5 Conclusions

The results obtained in this section revealed the optimum conditions for the accelerated carbonation of APCr. Three fundamental parameters for the success of the reaction have been studied, the reaction time, the water content of the ash and its particle size. This information set the basis for the study of the kinetics of carbonation of APCr.

The kinetic model ascertained for carbonation of APCr, Holt-Cutler-Wadsworth model, agrees with others found in the literature for systems of similar nature. The selection of the model was also supported by mineralogical and micro-structural analysis.

This work fulfils the main objective of this thesis that is, optimising the major parameters determining the extent of carbonation of MSWIr and modelling the carbonation reaction of APCr therefore, providing a fundamental understanding of accelerated carbonation for the treatment of MSWIr.

CHAPTER 7

7 Commercial Feasibility Study

7.1 Introduction

The aim of this Chapter is to assess the business opportunity deriving from Accelerated Carbonation in the UK. Carbonation has the major advantage of permanently binding CO_2 with waste materials whilst producing re-usable artificial aggregates. At a time when rapidly changing legislation is promoting the recycling and reuse of waste materials, the emergence of sustainable waste management technologies that can utilise both gaseous and solid waste products in re-useable materials is timely.

The principal objective of the joint project described in 1.1 is to investigate and optimise the potential for accelerated carbonation of silicate-based municipal wastes using waste CO_2 to produce artificial construction aggregates. The continuing research at University of Greenwich involves the determination of the short and long term chemical properties of the MSWIr after carbonation, with particular interest in the leaching behaviour and the potential to produce reusable artificial aggregates potential. For the study reported in this Chapter it is assumed that carbonation converts MSWIr in reusable secondary aggregates.

The options for the commercial application of Accelerated Carbonation to a number of different markets were studied. Following this market analysis, major competing innovations were compared. The final step was to find the most economically viable and sustainable business model for implementation among the various options.

Since the technology has been proven on a pilot plant scale over the last few years [33-35, 122] for different kinds of wastes and contaminated soils (see Table 2-2), the commercial feasibility of Accelerated Carbonation requires investigation.

The *New Technology Ventures* course at London Business School provided a forum for this feasibility study. In this chapter, the approach to business feasibility evaluation developed by John Mullins [123] has been applied in presenting the findings and recommendations. The framework divides the feasibility analysis into five core areas. Four are shown in Table 7-1. The fifth one is the management team, which has not been considered in this analysis. The difference between market and industry is the one of demand and supply.

	MARKET	INDUSTRY
Macro-level	No. of customers and aggregate money spent. Future market growth & attractiveness.	Is the industry structurally attractive? Likely changes therein going forward.
Micro-level	Target market segment size and growth rate. Identify the benefits of the solution. Options to grow into other segments.	Proprietary elements? Capabilities identified that are not easily duplicated. Economic viability of business model.

Table 7-1 Framework behind the feasibility study

The market refers to the customer, or potential target customers and their needs, whereas the industry refers to sellers that offer products or services that are similar or close substitutes for one another and how the venture will be able to capture value within the relevant sector. An analysis of these four areas should highlight and quantify available opportunities in the UK.

Table 7-2 summarises the range of applications of Accelerated Carbonation as described in Chapter 2.

Application	**Description**
Accelerated curing of cementitious systems	When applied to compacted systems, after 3 minutes of carbonation the amount of cementitious components reacted is ~ equivalent to that after 12h of hydration.
Stabilisation/ solidification technique	Cement-based solidification using binders is used for the immobilisation of soils and sludges containing a variety of metal pollutants.
Stabilisation of wastes	There is a wide range of waste materials with potential for Accelerated Carbonation (see Table 2-1).
Stabilisation of contaminated soils	The contamination in derelict land can be treated using waste CO_2, carbonating with it a mixture of the contaminated soil and an appropriate binder. The major advantage over conventional systems is that the soil is immediately available for development.
Recycling of waste streams	Treatment of non-hazardous waste streams to improve their reuse in some way. For instance, powdered materials with appropriate properties could be solidified to produce useful products or the recycling of concrete waste produced by demolition.

Table 7-2 Applications of Accelerated Carbonation

7.2 Macro Market: Market selection

Accelerated Carbonation is applicable to a number of different markets in the UK. The size, legislative pressures, trends and relative growth rates of the identified markets were examined in order to determine which would be most appropriate for initial market entry.

The three most promising targets include:

- Waste management companies that can incorporate Accelerated Carbonation
- Companies that generate CO_2 emissions
- Companies that treat/remediate contaminated land

7.2.1 Legislation and Trends

A wide range of legislation from both the EU and UK is increasingly affecting these markets. The most important are shown in Table 7-3:

Legislation	Main factors affecting the market
Landfill tax	▪ Has been steadily increasing and reached £15/t by April 2004. ▪ The government intends to increase this up to £35/t in the coming 10-year period. ▪ The number of landfill sites is being reduced from 200 to 10.
CO_2 emissions	▪ Kyoto Protocol: Ratified by the EU in 2002 and by Russia in Nov 2004. The target in the EU is to cut greenhouse gases to 8% below the 1990 level by 2008-2012. The UK goal is 20% reduction by 2010. The protocol, committing 30 industrialised countries became legally binding in Feb 2005. ▪ DTI Energy White Paper: In 2003 the UK committed to 60% reduction of emissions by 2050, following the advice of the Royal Commission on Environmental Pollution. ▪ MSW incinerators in the UK are currently not taxed but it is likely that this will change due to intense international pressure to adhere to stated targets.
Aggregates Levy	▪ Came into force in April 2002 as a way to incentivise recycling of aggregates. A levy of £1.60/t is taxed on natural aggregates mined in the UK. ▪ Secondary aggregates resulting from Accelerated Carbonation waste are exempt and this legislation therefore skews the economics in their favour. ▪ In the UK, recycling of BA is not so well developed in comparison to most EU countries. For example, in The Netherlands 100% of BA is reformed as aggregates and this figure is 50% in both France and Germany.
Contaminated land	▪ There is little legislation in terms of government targets but recent laws state that local authorities have a duty to identify any contaminated land and ensure effective remediation. ▪ The polluter, if identified, must bear the full cost and responsibility of remediation for any land that they have polluted.
Hazardous wastes	▪ The co-disposal of hazardous and non-hazardous waste is banned since July 2004. ▪ The pre-treatment of hazardous wastes prior to disposal is now compulsory. In addition, from July 2005 the Waste Acceptance Criteria (WAC) will determine the pre-treatment requirements. ▪ There are 250 additional items that have been classified as hazardous.

Table 7-3 Legislation affecting the market for Accelerated Carbonation

7.2.2 *Market 1 – Waste Management Companies that can Incorporate Accelerated Carbonation*

The estimated waste management market will grow by 32.3% between 2002 and 2007 to reach £6.1bn [61]. PFA, BFS and MSWIr were selected for closer analysis as target waste streams for the commercial application of ACT, on the basis of volumes produced, degree of hazard and reactivity to CO_2. (More details on these wastes were given in Chapter 3).

By considering current disposal routes, BFS was disregarded because more than 75% of the (relatively small) volume produced (0.6 Mt/yr) is already recycled. However, the steel industry expects to pay high taxes for their CO_2 releases in the near future. This would make a stronger case for the Accelerated Carbonation of steel slag, which would treat both of their major waste streams simultaneously.

In terms of reactivity, PFA (5.5 Mt/yr) has been shown to react relatively poorly to Accelerated Carbonation [61]. As more than half of PFA is currently reused in the construction industry due to its harmless nature, it has been disregarded as an early target for commercial application of Accelerated Carbonation. However there may be opportunities as a treatment process to refine the physical characteristics of this material.

As mentioned in Chapter 3, currently there are 30Mt of MSW being produced per year in the UK [2], over 80% of which is directly disposed of in landfill sites in the UK. Approximately 10% of MSW is recycled and a further 10% is incinerated. The ashes produced from incineration (~3.0Mt/yr) are landfilled to a large degree, though some are reformed and reused as secondary aggregates [3]. Compared to BFS or PFA, MSWIr are particularly difficult to reuse. 79% and 88% of the BA and APCr respectively, are currently sent to landfill sites. However, BA and APCr react well through carbonation (see Figure 3-1). Opportunity therefore exists for waste management companies to increase incineration and reduce landfilling through the subsequent production of secondary aggregates using this technology. For these reasons, MSWIr are considered as a logical target for early application of Accelerated Carbonation.

There is strong legislative pressure to reduce landfilling in the UK in the face of increasing MSW volumes. Additional pressure to reduce CO_2 emissions in line with the Kyoto Protocol is likely to cause the government to introduce levies on waste incineration in the coming years. A market for which a technology such as Accelerated Carbonation has a strong potential impact, given that it is a process that sequesters CO_2 into materials with engineering properties that would otherwise be landfilled at cost.

7.2.3 Market 2 - Companies that Generate CO_2 Emissions

In the UK, 550 Mt of CO_2 is released into the atmosphere each year [13]. The main emitters are power stations (29%), road transport (21%) and domestic producers (16%). Though CO_2 emissions are shrinking slightly, further reduction of 18.3Mt/yr of the current emissions is required to achieve the earliest Kyoto targets. Thus there is a need for both the reduction and capture/storage of CO_2. Assuming a high efficiency Accelerated Carbonation process with 50% wt. CO_2 capture, a further 20 Mt of aggregates would need to be produced each year to hit targets set by the Kyoto protocol. This is unrealistic, both because it would require a large increase in the volume of secondary aggregates being produced and because the costs of CO_2 capture and transport are very high. The predictions point at this cost being around £34/tCO_2 by 2020/25 [124]. Therefore, power stations would need to be targeted, yet they do not produce ash that has high CO_2 absorption capacity. The impracticalities and expected high costs of this situation make this market currently unattractive, although there may be other chemical processes where the available waste streams make this application more economically favourable (e.g. titanium dioxide production).

7.2.4 Market 3 - Companies that Treat/remediate ContaminatedLand

In 2001, the UK market value for contaminated land remediation was estimated at £470m/yr. This represents a rise of 23% in the past four years [125], and growth is expected to continue at double digit rates through 2006. The Environment Agency estimates that there could be as many as 5,000-20,000 contaminated sites in England and Wales [126]. There are several applicable techniques that are currently being used for land remediation (see Table 7-4):

Remediation Technology		Cost (£/ton)	Treatment time/ton
Vacuum extraction	Uses hot-air injection or electric/radio frequency heat to increase mobility of semi-volatiles and facilitate extraction	40	3- 6 months
Biotreatment	Based on accelerating the natural degradation of environmental contaminants by micro-organisms	50	3- 6 months
Chemical	Addition of chemicals to the ground	100	6-12 months
Solidification	Addition of cement and hydration of the mixture	110	1-3 months
Thermal treatment	Despite avoiding digging and transport costs is an expensive process.	180	6-12 months
Accelerated Carbonation	Addition of cement and carbonation of the mixture	30	< 1 day

Table 7-4 Comparative costs of remedial options for contaminated land [127]

The one of the most significant growth sectors within the contaminated land remediation market during the review period is believed to be bioremediation, which is estimated to have risen to market shares of 7% in 2001. The main benefits of Accelerated Carbonation in this market are that it is a simple application and the treated land is ready for redevelopment on the same day. The market for contaminated land treatment is significant and growing. Given the great savings, both in costs and treatment time, the belief is that this is a suitable niche for market entry.

7.2.5 Macro Market Summary

Overall trends and legislation favour Accelerated Carbonation, particularly due to the enormous constraints being placed on landfilling. In addition, there is significant growth in the majority of the applicable markets analysed, which is clearly an attractive environment in which to launch a new venture. Finally, the waste management market and MSWIr sub-segment and the soil remediation have been identified as being particularly suitable for application of the technology. The rest of this study is therefore focused on exploring the exploitation of Accelerated Carbonation in the treatment of MSWIr since the threat of rivalry and substitutes is lower. Contaminated land remediation is considered an ideal possibility for further expansion.

7.3 Micro Market: Target Customer

Within the chosen waste management area, the benefits of Accelerated Carbonation apply to three key target customer groups, namely MSW incinerators, MSWIr processing companies and aggregate manufacturers.

7.3.1 Group 1 - Municipal Solid Waste Incinerators

There are 15 incinerators in UK, 7 under construction, and another 17 proposed or in the planning process. Once they are completed, the total capacity of the UK's incineration industry will more than double from 2.9Mt/yr to 7.2 Mt/yr [4], sufficient to accommodate 25% of the UK's municipal waste and reduce landfilling significantly. Although incineration reduces waste volume by 90%, when performed on this scale it will generate high volumes of ash. No longer will incinerators be able to afford sending most of their resultant waste directly to landfill sites. Increasingly, they will look to waste management companies to treat their waste to avoid landfill charges.

One possible business model is to sell or license the Accelerated Carbonation process to incinerators directly. In this manner, they would be able to build their own carbonation plant and sell their carbonated ash to aggregate manufacturers for further processing and/or resale. The primary benefits that carbonation offers this group include:

- Avoiding landfill taxes
- Increasing the resale value of their waste ash
- Avoiding costly processing/disposal of hazardous waste

CO_2 sequestration does not result in direct savings for MSW incinerators because they are currently not charged for their CO_2 emissions.

7.3.2 Group 2 - MSWIr Processing Companies

APCr processing companies have not been considered in the micromarket analysis given that most of the APCr are currently sent to landfill. Looking forward, the new landfill legislation will lead to the development of a market for APCr processing.

Presently, there are two companies dealing with all the BA produced in the UK, Ballast Phoenix and Onyx Hanson. They rely upon natural carbonation, a process that requires more time and physical space than Accelerated Carbonation and yields lower quality aggregates. The landfill tax will drive-up the amount of ash that is produced and, consequently, the demand for processing and reuse. Given the amount of time and land required by present processing methods, these companies will encounter significant challenges handling the high volumes of incinerated waste expected in the future. Similarly, the environmental restrictions imposed on secondary aggregates limit demand for aggregates produced through natural weathering.

For this reason, these two companies landfill a significant percentage of their secondary aggregates and sell what they can at a very low price. Accelerated Carbonation can benefit these waste management companies by:

- Decreasing the treatment time from 6 months to a few hours
- Removing the need for large areas of land in which to process waste
- Improving the quality of secondary aggregates (physical properties, toxicity) resulting in a higher sale price than naturally carbonated ash.

However, in order to implement the technology economically, these companies will probably need to physically process aggregates at the incinerator locations. Currently, the MSWIr is transported from incinerators; they do not process it onsite. Therefore, they will have to secure agreements with incinerators to incorporate Accelerated Carbonation facilities into the plants or build/purchase Accelerated Carbonation-enabled incinerators

7.3.3 Group 3 - Aggregate Manufacturers

It is estimated that the demand for secondary aggregates in the UK is 18 Mt/yr, representing 22% of the aggregate market [128]. In all likelihood, construction companies will become increasingly interested in secondary aggregates because of the penalties and restrictions being placed on the use of natural aggregates. However, current BA processing methods do not produce materials of the quality and safety that widespread commercial use requires. Figure 3-5 shows current uses of BA after processing. Aggregate production from APCr is not considered due to the limitation imposed by the Environmental Agency on passing treated hazardous wastes as non hazardous building materials. Aggregate production from APCr is limited by the high chloride content and the leaching behaviour of the treated material.

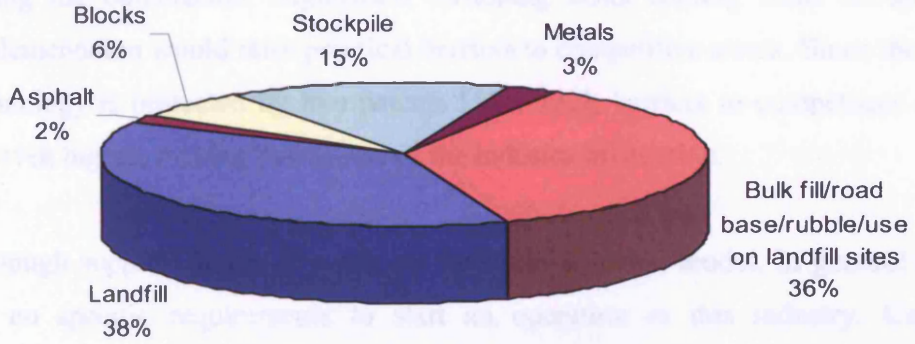

Figure 3-5 Uses of BA after processing (1996-2000) [129]

Though various checks and approvals may be required to increase secondary aggregate sales, Accelerated Carbonation can clear this hurdle by producing aggregates that are:

- Cheaper than natural aggregates
- Of better quality than the currently produced secondary aggregates, allowing wider usage

7.3.4 Micro Market Summary

There are a number of different target markets within the waste management area for the technology. Each of the markets could feasibly be targeted, but the incinerators make an ideal entry point for commercial Accelerated Carbonation

implementation by adding a carbonation plant to their existing facilities. A primary reason for this is that both ashes and CO_2, the main components of the treated aggregates, are produced on site, which brings immediate efficiencies and scale benefits.

7.4 Macro Industry: Industry Potential

Porter's Five Forces framework [130] has been used to analyse the industry for waste management using Accelerated Carbonation. Figure 7-2 shows the Five Forces diagram for this industry. Each of the forces is discussed in turn below.

As discussed above, the best option for early implementation of Accelerated Carbonation would be an energy efficient incineration-carbonation integrated plant in which the solid wastes would be carbonated with the CO_2 generated during the combustion. Significant switching costs coming from set-up and implementation would raise practical barriers to competitive attack. Since the core technology is protected by two patents [131, 132], barriers to competitors entry are even higher, making this aspect of the industry favourable.

Although supplier power depends on the exact business model, in general there are no specific requirements to start an operation in this industry. Capital, equipment and human resources are all available from a variety of sources. The most important input into the industry, i.e. the technology and tacit knowledge related to it, is restricted to a few people and organisations, making supplier power favourable.

With regards to substitutes, it must be noted that there is no standard and/or widely adopted technology by the industry. Moreover, current legislation and taxation, with a strong emphasis on reducing landfill and energy consumption, as opposed to direct measures to reduce greenhouse gas emissions, favours a technology such as Accelerated Carbonation. However, if the favourable government policies and tax measures were reversed, this would have a major impact on the commercial attractiveness of Accelerated Carbonation. As, any such reversal is unlikely, the threat of substitutes is assessed as relatively low.

Rivalry is currently low as there are no direct competitors to Accelerated Carbonation. There are other research groups in the UK applying carbonation to treat cement-based wastes but mostly at academic level. In the EU there are few small companies researching the use of carbonation to treat MSW BA. However, the projected growth of the market will allow space for several commercial entities to make a profit and therefore competition is not expected to be particularly intense.

The final element of Porter's five forces is the most unattractive side of the industry, the power of buyers. Within the chosen segment, only a few big players are the potential customers. Despite the fact that significant growth is expected in the market, the actual number of buyers will probably not increase much, potentially making the current buyers even stronger. Finally, the monetary value extracted from Accelerated Carbonation lies in reducing landfill taxes and revenues from aggregates resale. The issue of how the value created is split between the patent holder and the buyers, is largely a contractual negotiation. This threat can be reduced by overseas expansion to escape the UK oligopoly of buyers.

Figure 7-2 Five Force Analysis of the waste management industry

7.4.1 Macro Industry Summary

Of the five forces, buyer power is considered the most threatening but nonetheless manageable. Since the other forces are generally in favour of Accelerated Carbonation, overall this technology is in a favourable position to enter the waste management industry.

7.5 Micro Industry: Business Model

When commercialising a technology, consideration needs to be given both to immediate returns as well as sustaining competitive advantage over time.

Immediate returns are dependent on the form and terms of commercialisation (joint venture, technology licensing, consulting, etc.), number of customers and costs incurred. Assuming integrated Accelerated Carbonation facilities were installed alongside a typical MSW incinerator, early estimates of landfill savings and revenues from sales of aggregates show attractive returns after allowing for set-up investment and on-going running costs (see Section 7.5.1.3).

Over time, protecting Intellectual Property (IP) and continuing to invest in R&D to remain at the forefront will ensure a strong competitive position and further drive revenues. The resolution of these issues will crucially determine the success of the technology in the long term.

7.5.1 Business Model Selection

In this section, three examples of business models for the selected market are explored. To evaluate these options there are two main factors to be considered: appropriation of economic benefit and time-to-market. Timing is very important because the industry is looking to apply viable options before landfilling restrictions come into force.

7.5.1.1 Licensing

Model: Operate an IP and research company that licenses the process technology. The fee structure could be in the form of a fixed annual licence fee or a variable royalty.

This is the easiest business model. The risks and capital requirements are low, but consequently a smaller share of the economic benefits could be captured. In addition, it raises questions on the sustainability of the business in the long term. A continuous Research & Development activity should be maintained in order to be competitive against emerging technologies.

7.5.1.2 Joint Venture

Model: Establish a partnership with a waste management company to build Accelerated Carbonation-enabled incinerators and modify existing plants. The profits generated would be shared according to an agreed formula.

This model suffers from a time-to-market weakness and may require significant capital investment. On the other hand, this business model is very attractive from a mid-term perspective since the market is large and has to be addressed as fast as possible. Finally, it offers the possibility of getting higher revenues from long term contracts. At the same time, this would be dependent on the company's ability to negotiate effectively with large waste management companies that could be in a superior bargaining position.

7.5.1.3 Spin-out

Model: Create a separate company[5] holding the IP and further develop this into an engineering/consulting company. The early commercial focus would be on MSW incinerators and, over time, it could expand to other markets.

A quick entry into the market can be achieved by providing a consulting and solution engineering for any of the potential customers. This model would require modest capital and could provide both up-front and recurring revenues. Furthermore, by not relying on any one customer, the company would improve its negotiation position.

Much of the reasons behind the economic viability of running an Accelerated Carbonation plant by an incinerator lie in the high future costs of landfilling.

[5] A spin-out is a company which is set up as its own entity by a university or a larger company typically to make commercial use of a new technology that has been developed in research.

Calculations based on estimates showed that an incinerator could obtain an extra annual profit of ~ € 2.6m with an operational carbonation plant. Appendix 3 shows the calculations, based on best estimates, analysing the viability of this business model on the initial target market.

Given the significant benefits that Accelerated Carbonation offers incinerators, the spin-out company could charge for the design, engineering and integration of the plant. The company could also charge a significant annual licence fee for the technology which could be based on a percentage of the client's annual cost savings. Looking forward, the spin-out company could sell to other incinerators outside the UK or into other markets, such as land remediation.

7.6 Conclusion

Based on the analysis it can be concluded that Accelerated Carbonation is an exciting opportunity to address a number of increasingly urgent environmental issues. If there is ever a time to commercialise the technology, it is now.

Accelerated Carbonation can be applied to several different markets. The best opportunities are land remediation and stabilisation of MSWIr. However, the short-term choice is carbonating MSWIr. These residues are relatively easy to carbonate and capture a significant amount of CO_2. MSW is one of the largest waste streams in the UK and is expected to double in the next fifteen years [133].

Just as there are several market opportunities, there are also multiple business models that can be used to extract value generated by the technology. Based on time to market and appropriation of the economic benefit, the spin-out business model is recommended. The analysis shows that, by applying Accelerated Carbonation to an average MSW incinerator, value in excess of € 2.6m/yr could be generated. Once established, the new venture must continue to invest in research and development to build a sustainable market position.

NOTE: This technology has now been spun out into a commercially operating company known as Carbon8 Technologies Ltd.

CHAPTER 8

8 Conclusions and Future Work

This thesis has focused on studying major parameters governing Accelerated Carbonation of Municipal Solid Waste Incinerator Residues (MSWIr) and has discussed their influence on the reaction kinetics of Air Pollution Control Residues (APCr) (Chapter 6). In addition, an in depth commercial feasibility study has shown the value that could be generated by the commercial application of the technology (Chapter 7).

The application of carbonation has been studied in the past for the treatment of MSWIr. The studies have been mostly concentrated on the influence of carbonation of MSWIr on metal mobility and leaching behaviour. However, the modelling of the carbonation reaction has not received the same attention in literature. The experimental work of this thesis has therefore focused on the effect of the reaction conditions on the rate of carbonation.

8.1 Conclusions

The effects of carbonation on the properties of cementitious materials are different. Despite the known adverse effect in some systems, in many cases the outcome may be beneficial. There is a growing interest in the potential of Accelerated Carbonation to provide a way of sequestering CO_2 as a solid salt in a variety of treated products, reducing landfill waste volumes and resulting in materials that can be re-used, for example, as construction aggregates.

The application of Accelerated Carbonation for the treatment of MSWIr has been examined in this study. The use of incineration for MSW disposal continues to grow as landfill space decreases. Thus in the future there will be large volumes of combustion wastes available. Due to their composition and high content of lime they are suitable for reaction with CO_2 through Accelerated Carbonation. This process imparts chemical and mineralogical changes on the ashes, which reduces their harmful environmental impact through the encapsulation of hazardous

components and cementation by carbonate precipitation. The reduced hazard and stabilised nature of the carbonated MSWIr gives them potential to be used as secondary construction materials.

As a first approach to the Accelerated Carbonation of incinerator ashes, three fundamental parameters for the success of the reaction have been studied, namely the reaction time, the water content of the ash and its particle size. The optimum values obtained were the following:

- Optimum reaction time for BA and APCr is 2.5 h.
- Carbonation is better for smaller particle size. Considering the particle size distribution of MSWIr, the fractions below 710 μm and 212 μm for BA and APCr respectively, have been selected as the optimum for carbonation.
- The optimum water-solid ratio for the selected size fraction is 30-40% for BA and 20-30% for APCr.

As a result of carbonation there is a clear change in mineralogy and morphology of the ash showed by XRD and SEM analysis. The carbonated product is a denser solid of lower porosity with calcite infilling the pore space.

This information sets the basis for the study of the kinetics of carbonation of MSWIr, fundamental for the understanding and modelling of the process. Once modelled, it will be possible to optimise the parameters required for the design of a continuous process at larger scale.

The kinetics of carbonation of APCr were studied at temperatures from 10°C to 60°C using a batch reactor. Experiments were run for 3h after which the conversion of $Ca(OH)_2$ contained in the APCr was incomplete. The main conclusions regarding the kinetics of carbonation of APCr were:

- The concentration of CO_2 and the water-to-solid ratio are variables governing the rate of carbonation of APCr.
- The reaction is dependent on the temperature but is zero order with respect to relative humidity.

- Carbonation is better for heterogeneous samples of wide size range due to the higher voidage.
- The carbonation of APCr is a diffusion-controlled reaction.
- The carbonation of unclassified APCr at 3 bars in a 5 litre batch reactor at 65% relative humidity, temperatures between 10 and 60°C, concentration of CO_2 from 10% to 100% and w/s from 0.2 to 0.4, fits the Holt-Cutler-Wadsworth model for diffusion-controlled reactions. Equation (6.13) shows the ascertained kinetic model:

$$\frac{d\alpha}{dt} = 0.1394 \exp\left(-\frac{8.186}{RT}\right) \cdot \frac{-1}{\ln(1-\alpha)} \qquad (6.13)$$

- When carbonating more homogeneous fractions of APCr at the same reaction conditions stated above, the carbonation is best modelled by the Ginstling-Brounshtein model for diffusion controlled reactions.
- The reaction proceeds through the surface of the particles of APCr as calcium ions that are dissolved in the water are consumed to form $CaCO_3$.
- The reaction is quite slow because it only occurs in a very thin layer of water that covers the particles. As carbonation proceeds, the product particles precipitate on the surface of the APCr and build up a thicker product layer that increases the resistance to the penetration of CO_2.

The models ascertained for carbonation of APCr agrees with others found in the literature for systems of similar nature [49, 92, 97, 98, 112]. The selection of the models was also supported by mineralogical and micro-structural analysis.

The commercial feasibility of the Accelerated Carbonation of MSWIr has also been studied due to the great potential of this technology to address important environmental problems. Considering the market and industry for sustainable waste management and the capacity of Accelerated Carbonation to enable the recycling and reuse of CO_2 and solid wastes, there is a great and immediate potential for the commercialisation of Accelerated Carbonation technology. It is mostly favoured by the recently imposed rise in CO_2 and landfill taxes and the increase of waste generation in the UK.

A spin-out venture focused on marketing and licensing the technology combined with consulting/engineering services for implementation would be the most appropriate business model, assuming low capital availability. The main advantages of this choice include low up-front investment requirements, the ability to act quickly, recurring annual revenue stream from licensing and the ability to pursue wider market opportunities over time.

8.2 Future Work

8.2.1 Improvement to the Quality and Extent of Carbonation

Regarding the improvement of the extent of carbonation, tests could be carried out comparing the effect of different process set-ups or solid pre-treatments. The following are some examples of what these could be:

- Given the observed increased leachability of anions in the carbonated APCr as published in [134], an area for potential future work would be to study the possibility of a slight washing step prior to carbonation to remove the chlorine. This APCr pre-treatment step has been carried out in similar stabilization/solidification methods [80].
- It is an ancient practice to wet and then dry lime mortar to improve its carbonation. Wetting and drying is known to detach the outer layer of carbonated material from the inner uncarbonated one. This is explained by the fact that portlandite is more soluble than the calcite layer, so that when water reaches the interface, detachment can occur. When no CO_2 impermeable layer could be formed, the possibility to reach full carbonation is thus improved [95]. Further studies could be carried out implementing wetting and drying cycles to enhance the reactivity of the solid.
- Carbonation could be carried out under dynamic conditions. The reaction could be further accelerated by passing the CO_2 containing gas through a bed of materials rather than relying on diffusion. Previous experiments have been completed at the University of Greenwich shaking the vessel throughout the reaction to attain dynamic conditions [134]. Carbonation could also be improved by using a rotary carbonation chamber, in which the particles would break one another and favour carbonation by presenting more fresh surfaces to

the gas. This would improve the mass and heat transfer, speeding up the reaction kinetics.

8.2.2 Kinetics

In order to get more insight about the reaction kinetics of APCr with CO_2, an advanced model should be developed valid for a wider range of reaction conditions. Factors such as the degree of carbonation and the difference in penetration of CO_2 in different zones, the possible interaction between the water liberated during carbonation and the APCr should be taken into account in the advanced model. In addition, a non-dimensional parameter could be defined and included in the model to describe the solid characteristics.

Carbonation of MSWIr is quite a complex process. The description of the system in terms of a pair of Arrhenius parameters and a single reaction model is a good and simple first approach. Other possible future work would be to consider multi-step kinetics to analyse this system using, for example, the isoconversional model or the "non-parametric kinetics" (NPK) method [115].

The carbonation reaction of the $Ca(OH)_2$ has been the focus of this kinetic study. Another area of future work could be to analyse the effect of carbonation on the silicate components of the APCr. The combination of the two would give a more complete analysis of the accelerated carbonation reaction of APCr.

8.2.3 Carbonated Ash as Secondary Aggregate

The incorporation of waste in concrete manufacture may provide a solution to the increasing problems of waste management. The construction industry uses large quantities of natural materials. Therefore, its capacity to recycle and upgrade waste is considerable. Industrial by-products such as fly ash, silica fume, etc. have been used for years as cement and concrete components. Carbonated APCr have potential to be recycled and upgraded in concrete.

In order to ensure the new material is usable as a building material and that satisfies the specifications determined by its applications it must be tested for:

- performance characteristics i.e. workability, mechanical strength, etc.
- influence in concrete durability
- environmental impact of the new material

Therefore, possible future work would be to evaluate and optimise the effects of the incorporation of carbonated APCr in concrete and cement. The effect of reaction conditions on these properties could also be studied.

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Appendix 1

Waste Management in UK (tonnes/year)

Catalogue no.	Name	Incineration without energy recovery	Landfill	Recycling/Reuse	Waste Transfer	Treatment	Total
10 01 00	**Wastes from power station and other combustion plants**						
10 01 01	Bottom ash		20,106.40		15.79		1,400,000
10 01 02	Coal fly ash		3,100,000	2,000,000			5,100,000
10 01 03	Peat fly ash		20.44				20.44
10 01 04	Oil fly ash		369.26				369.26
10 01 05	Calcium based reaction wastes from flue gas desulphurisation in solid form		2,778.7		8.32	340.42	3,127.44
10 01 06	Other solid wastes from gas treatment		62.87		0.87		63.74
10 01 07	Calcium based reaction wastes from flue gas desulphurisation in sludge form						21.12
10 01 08	Other sludges wastes from gas treatment						2.40
10 01 09	Sulphuric acid						32.00
10 01 10	Spent catalysts, e.g. from removal of NOX						
10 01 11	Aqueous sludges from boiler cleansing		6.64			111.84	119.08
10 01 12	Spent linings and refractories		194.36			3.66	198.52
10 01 99	Wastes not otherwise specified	55.38	501.04	8.84	406.81	448.29	1,420.35
10 02 00	**Wastes from the iron and steel industry**						
10 02 01	Waste from the processing of slag				2.39		2.39
10 02 02	Unprocessed slag		242.62				242.62
10 02 04	Sludges from gas treatment				3.00		3.00
10 02 05	Other sludges		901.44	8.18	212.91	1.66	1,124.19
10 02 06	Spent linings and refractories		11,127.22				11,127.22
10 02 99	Wastes not otherwise specified	31.74	3,410.08	245.59	334.27	276.02	4,297.70
10 03 00	**Wastes from aluminium thermal metallurgy**						
10 03 01	Tars and other carbon-containing wastes from anode manufacture		444.38				444.38
10 03 02	Anode scraps				13.12	24.60	37.72

Catalogue no.	Name	Incineration without energy recovery	Landfill	Recycling/Reuse	Waste Transfer	Treatment	Total
10 03 03	Skimmings		28.82	648.04	43.33		720.19
10 03 04	Primary smelting slags/white drosses		26.14	2,614.81	1,473.71	10.66	4,125.32
10 03 05	Alumina dust		2.74				2.74
10 03 06	Used carbon strips and fireproof materials from electrolysis		66.02				66.02
10 03 07	Spent pot linings		5,321.38				5,321.38
10 03 09	Salt slags from secondary smelting		2,338.87	8,519.01	16,312.70		27,170.58
10 03 10	Black drosses from secondary smelting		19,343.02				19,343.02
10 03 11	Waste from treatment of salt slags and black drosses treatment		771.03				771.03
10 03 12	Flue gas dust		14.25				14.25
10 03 13	Other particulates and dust (including ball mill dust)		1,893.96				1,893.96
10 03 99	Wastes not otherwise specified		5,225.97	493.25	45.58	294.65	6,059.45
10 04 00	**Wastes from lead thermal metallurgy**						
10 04 01	Slags (first and second smelting)		25,639.62	1,430.50			27,070.12
10 04 02	Dross and skimmings (first and second smelting)			8,281.72	73.57	0.55	8,355.84
10 04 04	Flue gas dust		30.78	733.27			764.05
10 04 05	Other particulates and dust		1.86		80.96	44.10	126.92
10 04 07	Sludges from gas treatment				1,657.85		1,657.85
10 04 08	Spent linings and refractories		4.38				4.38
10 04 99	Wastes not otherwise specified			4,605.05	2.60	52.30	4,659.95
10 05 00	**Wastes from zinc thermal metallurgy**						
10 05 01	Slags (first and second smelting)		32.66				32.66
10 05 03	Flue gas dust		1,627.95		20.00		1,647.95
10 05 04	Other particulates and dust				1.31		1.31

Catalogue no.	Name	Incineration without energy recovery	Landfill	Recycling/Reuse	Waste Transfer	Treatment	Total
10 05 05	Solid waste from gas treatment		2.44		0.21		2.65
10 05 06	Sludges from gas treatment					93.31	93.31
10 05 07	Spent linings and refractories		47.71				47.71
10 05 99	Wastes not otherwise specified				23.24	22.01	45.25
10 06 00	**Wastes from copper thermal metallurgy**						
10 06 02	Dross and skimmings (first and second smelting)			0.50			0.50
10 06 03	Flue gas dust		401.84				401.84
10 06 05	Waste from electrolytic refining					15.06	15.06
10 06 07	Sludges from gas treatment		216.62				216.62
10 06 99	Wastes not otherwise specified				4.28	2.27	6.55
10 07 00	**Wastes from silver, gold and platinum thermal metallurgy**						
10 07 04	Other particulates and dust		13.43				13.43
10 07 05	Sludges from gas treatment		33.92		16.40	169.72	220.04
10 07 99	Wastes not otherwise specified		24.22		0.52	198.56	223.30
10 08 00	**Waste from other non-ferrous thermal metallurgy**						
10 08 01	Slags (first and second smelting)		89.64				89.64
10 08 02	Dross and skimmings (first and second smelting)		70	430.52	17.83	8.7	527.05
10 08 03	Flue gas dust		31.38				31.38
10 08 04	Other particulates and dust		2.16		0.21	0.34	2.71
10 08 05	Solid waste from gas treatment						-
10 08 06	Sludges from gas treatment						-
10 08 07	Spent linings and refractories		1,237.78		2.08	5.2	1,245.06
10 08 99	Wastes not otherwise specified		15.92		16.68	7.06	39.66

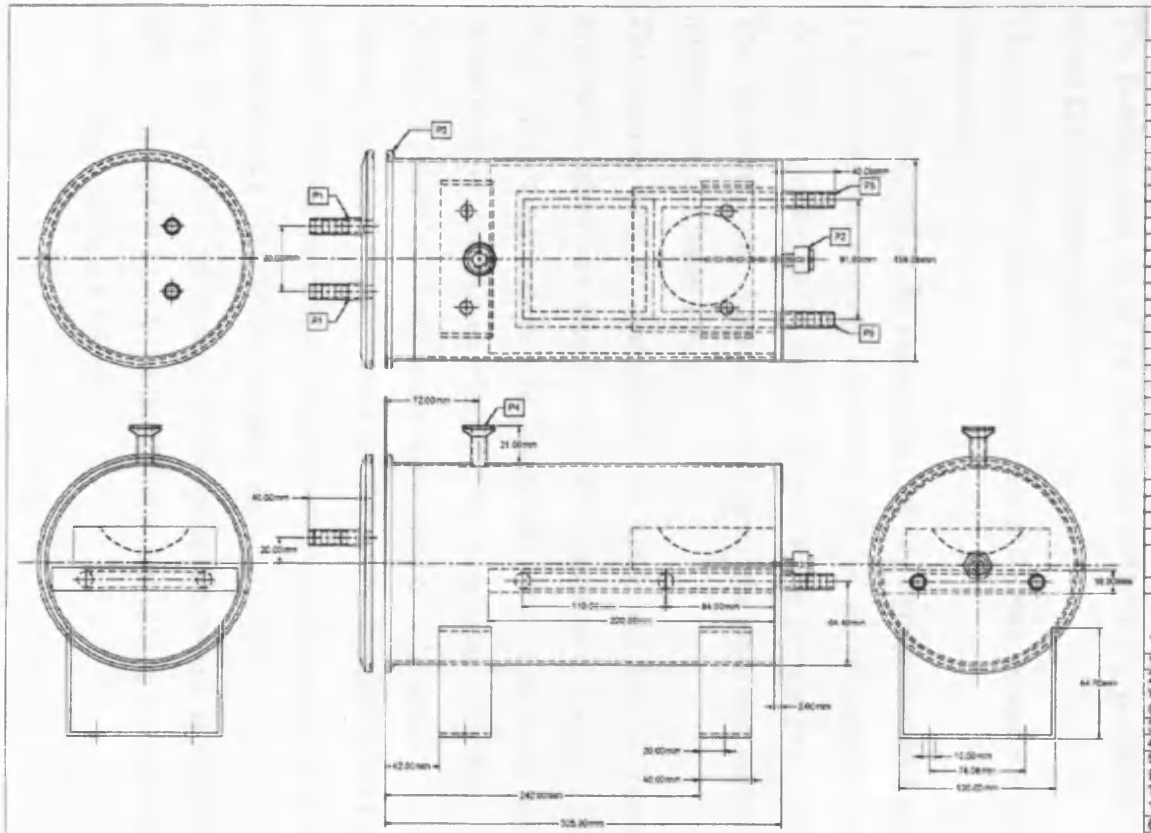
Catalogue no.	Name	Incineration without energy recovery	Landfill	Recycling/Reuse	Waste Transfer	Treatment	Total
10 09 00	**Wastes from casting of ferrous pieces**						
10 09 01	Casting cores and moulds containing organic binders which have not undergone pouring		26.78		5.12	6,914.47	6,946.37
10 09 02	Casting cores and moulds containing organic binders which have undergone pouring					9.06	9.06
10 09 03	Furnace slag		1,499,033.84	4,759,222			6,258,255.50
10 09 04	Furnace dust		5,635.39				5,635.39
10 09 99	Wastes not otherwise specified		406.9		7.30	32.08	446.28
10 10 00	**Wastes from casting of non-ferrous pieces**						
10 10 01	Casting cores and moulds containing organic binders which have not undergone pouring						
10 10 02	Casting cores and moulds containing organic binders which have undergone pouring		186.30				186.30
10 10 03	Furnace slag		1,000,000	3,000,000			4,000,000
10 10 04	Furnace dust		6.26				6.26
10 10 99	Wastes not otherwise specified		11.58				11.58
10 11 00	**Wastes from manufacture of glass and glass products**						
10 11 01	Waste preparation mixture before thermal processing		76.58		0.86	9.28	86.72
10 11 02	Waste glass				4.49	21.82	26.31
10 11 03	Waste glass-based fibrous materials				0.27		0.27
10 11 04	Flue gas dust		297.80			0.11	297.91
10 11 05	Other particulates and dust		16.30				16.30
10 11 06	Solid waste from gas treatment						

Catalogue no.	Name	Incineration without energy recovery	Landfill	Recycling/Reuse	Waste Transfer	Treatment	Total
10 11 07	Sludges from gas treatment			12.00	5.04		17.04
10 11 08	Spent linings and refractories		22.64		18.96	27.67	69.27
10 11 99	Wastes not otherwise specified	0.12	1847.22		34.88	326.71	2,208.93
10 12 00	**Wastes from manufacture of ceramic goods, bricks, tiles and constructions products**						
10 12 01	Waste preparation mixture before thermal processing				7.71	0.88	8.59
10 12 02	Flue gas dust		631.88				631.88
10 12 03	Other particulates and dust		189.28		3.02	20	212.3
10 12 04	Solid waste from gas treatment		3.26				3.26
10 12 05	Sludges from gas treatment				0.88		0.88
10 12 06	Discarded moulds		269.46		14.56		284.05
10 12 07	Spent linings and refractories						
10 12 99	Wastes not otherwise specified		1,317.38		30.8	616.71	1,964.89
10 13 00	**Wastes from manufacture of cement, lime and plaster and articles and products made from them**						
10 13 01	Waste preparation mixture before thermal processing						
10 13 02	Wastes from asbestos-cement manufacture		10.06		2.06		12.22
10 13 03	Wastes from other cement-based composite materials		284.84		12.90	20.00	317.74
10 13 04	Waste from calcination and hydration of lime		21.56				21.56
10 13 05	Solid waste from gas treatment						
10 13 06	Other particulates and dust						
10 13 07	Sludges from gas treatment						
10 13 08	Spent linings and refractories		485.34				485.34
10 13 99	Wastes not otherwise specified		11.48		5.81	93.50	110.79

Catalogue no.	Name	Incineration without energy recovery	Landfill	Recycling/Reuse	Waste Transfer	Treatment	Total
19 01 00	**Waste from incineration or pyrolysis of municipal and similar commercial, industrial and institutional wastes**						
19 01 01	Bottom ash and slag		6,507.69		5.55	25.29	6,538.53
19 01 02	Ferrous materials removed from bottom ash						
19 01 03	Fly ash		73,920		149	9,931	84,000
19 01 04	Boiler dust						
19 01 05	Filter cake from gas treatment		11,741.34				11,741.34
19 01 06	Aqueous liquid waste from gas treatment and other aqueous liquid wastes	1,176.05	417.09			4633.41	6,226.55
19 01 07	Solid waste from gas treatment		24,265.60		29.86	2772.24	27,067.70
19 01 08	Pyrolysis wastes						
19 01 09	Spent catalysts, e.g. from NOx removal						
19 01 10	Spent activated carbon from flue gas treatment						
19 01 99	Wastes not otherwise specified		98,251.98			16335.98	116,013.94

Appendix 2

Reactor Technical Drawing



Design Data	
Design Code	S.E.P.
Product Contact Material	316 Stainless steel
Welder Codes	BS EN288
Welder Procedures	BS EN 287
Operating Pressure	5 bar g
Sterilisation Pressure	N/A
Design Pressure	5 Bar g
Operating Temperature	4/151 Deg C
Sterilisation Temperature	N/A
Design Temperature	100 Deg C
Hydrostatic Test Pressure	TBA
Cooling Plate Op Pressure	0.5 bar g
Cooling Plate Design Pressure	N/A
Cooling Plate Operating Temp	N/A
Cooling Plate Design Temp	N/A
Cooling Plate Test Pressure	Leak Test Only
Cooling Plate Volume	63 ml
Contents - Vessel & Jacket	Non Hazardous
Corrosion Allowance	N/A
Vessel Working Volume	5 Litres
Nominal Total Volume	5 Litres
Nominal Vessel Weight	TBC
Nominal Total Weight	TBC
Internal Finish	240's grit, welds blended
External Finish	180's grit, welds Blended

Vessel Ports	ID
2 off 1/2" OD hose connectors for gas	P1
1 off 3.2mm ID compression for temp probe	P2
1 off 150mm ID tri clamp end port	P5
1 off 1/2" tri clamp for pressure gauge	P4
Heat Transfer Plate	
2 off 1/2" OD hose connectors	P5

General Notes

1) CUSTOMER TO SUPPLY REACTION DISH
2) DIGITAL PRESSURE GAUGE TO BE SUPPLIED WITH VESSEL. GAUGE TO HAVE A 1/2" TRI CLAMP CONNECTION AND NO DIAPHRAGM.
3) ALL SEALS WILL BE EPDM.
4) TEMPERATURE PROBE TO BE SUPPLIED WITH VESSEL.
5) COOLING PLATE IS SECURED IN THE VESSEL BY TW EXTERNAL FILLET WELDS ON THE 12MM WATER HOS TAIL CONNECTIONS. PLATE WILL ALSO REQUIRE TWO TACK'S TO SECURE ITS FRONT END.
6) ALL WELDS TO BE FULLY PURGED TIG WELDS.

5 LTR PRESSURE VESSEL

DRAWN BY	DJY
DATE	28.01.03
SCALE	DNS
DRAWING DATE	
PROJECTION	THIRD ANGLE

DRAWING NUMBER Y1276

Appendix 3

Economic Viability of Running a Carbonation Plant

In the analysis, the potential revenue and cost of implementing Accelerated Carbonation for MSWIr treatment were modelled. For this purpose, a number of assumptions were made as follows:

- A consulting and engineering company would design and construct the carbonation plant, which would be located next to the incinerator.
- The burning capacity of the incinerator is 500 kt/yr, producing 35 MW/h (size of the SELCHP incinerator).
- The CO_2, APCr and BA, electricity and other inputs are provided by the incinerator.
- CO_2 is transferred to the carbonation facility through standard piping.
- The carbonation process consumes 5% of the electricity produced by the incinerator and the rest is sold to the grid for an average price of € 37/MW.
- The Environmental Agency would give the spin-out permission for joint treatment of APCr and BA.
- The process uses a combination of APCr and BA to produce secondary aggregates, which can encapsulate 35% of their own weight of CO_2.
- There are no sub-products to be landfilled (100% of the ashes are treated).
- Investment in the Accelerated Carbonation plant has been conservatively estimated at €10m and would be depreciated over 10 years.
- Annual Operating Costs account for 20% of the annual Capital Costs.
- Annual General, Sales and Administration (GSA) amount to € 100,000 for the incinerator & € 200,000 for the spin-out.
- The total landfill cost savings for the incinerator would be € 50/tonne.
- 50% of aggregates have to be landfilled due to quality and low market demand.
- Price of aggregates is € 3/tonne.

Business case for the MSW incinerator

The business case for a MSW incinerator over the initial operational year is shown in Table A3-1. The Operating Profit of ~ € 2.6m shown below represents

the extra annual profit that the incinerator would obtain with an operational Accelerated Carbonation plant.

Revenues (€ 000's)		**Costs (€ 000's)**	
- due to avoiding landfill costs	4,200	- depreciation of plant	1,000
- due to avoiding carbon dioxide emission tax	0,0	- operating costs of plant	200
- due to selling aggregates	252	- GSA	100
		- energy costs of plant	518
Total	4,452	Total	1,818
Operating Profit	**2,634**		

Table A3-1 Business case for a MSW incinerator

This demonstrates a compelling business case for incinerators to incorporate the technology into their plants. A major reason for the economic viability of running a carbonation plant lies in the high future costs of landfilling.

Business case for the Spin-Out

The first five years projections of the income and expenses for the spin-out venture shows that this business case could lead to a viable and profitable company, as shown in **Error! Reference source not found.**.

	Year 1	**Year 2**	**Year 3**	**Year 4**	**Year 5**
Revenues (€ 000's)					
# of licenses	1	3	5	7	10
royalty fees[6]	0	60	180	300	420
consulting fees[7]	50	100	125	150	250
engineering fees[8]	0	1,000	1,000	1,000	1,500
Total	**50**	**1,160**	**1,305**	**1,450**	**2,170**
Costs (k€)					
GSA	200	200	200	200	200
# of employees	3	6	6	8	10
employee costs	150	400	500	600	800
Total	**353**	**606**	**706**	**808**	**1,010**
Net Income	**(-303)**	**554**	**599**	**642**	**1,160**

Table A3-2 Pro forma profit and loss account for spin-out venture

[6] 3% royalty fees of operating profit (estimated at € 2m) starting in first full year of operation of Accelerated Carbonation plant (year 2)
[7] € 50,000 per project in first 2 years, then increasing due to inflation and demand
[8] 5% of capital investment, first project not included

Appendix 4

List of publications

Publications

Fernandez Bertos M., Hills, C.D., Simons S.J.R. and Carey P.J., Production of Aggregates from Waste and CO_2, *Sustain' Magazine* 4(6) August (2003).

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